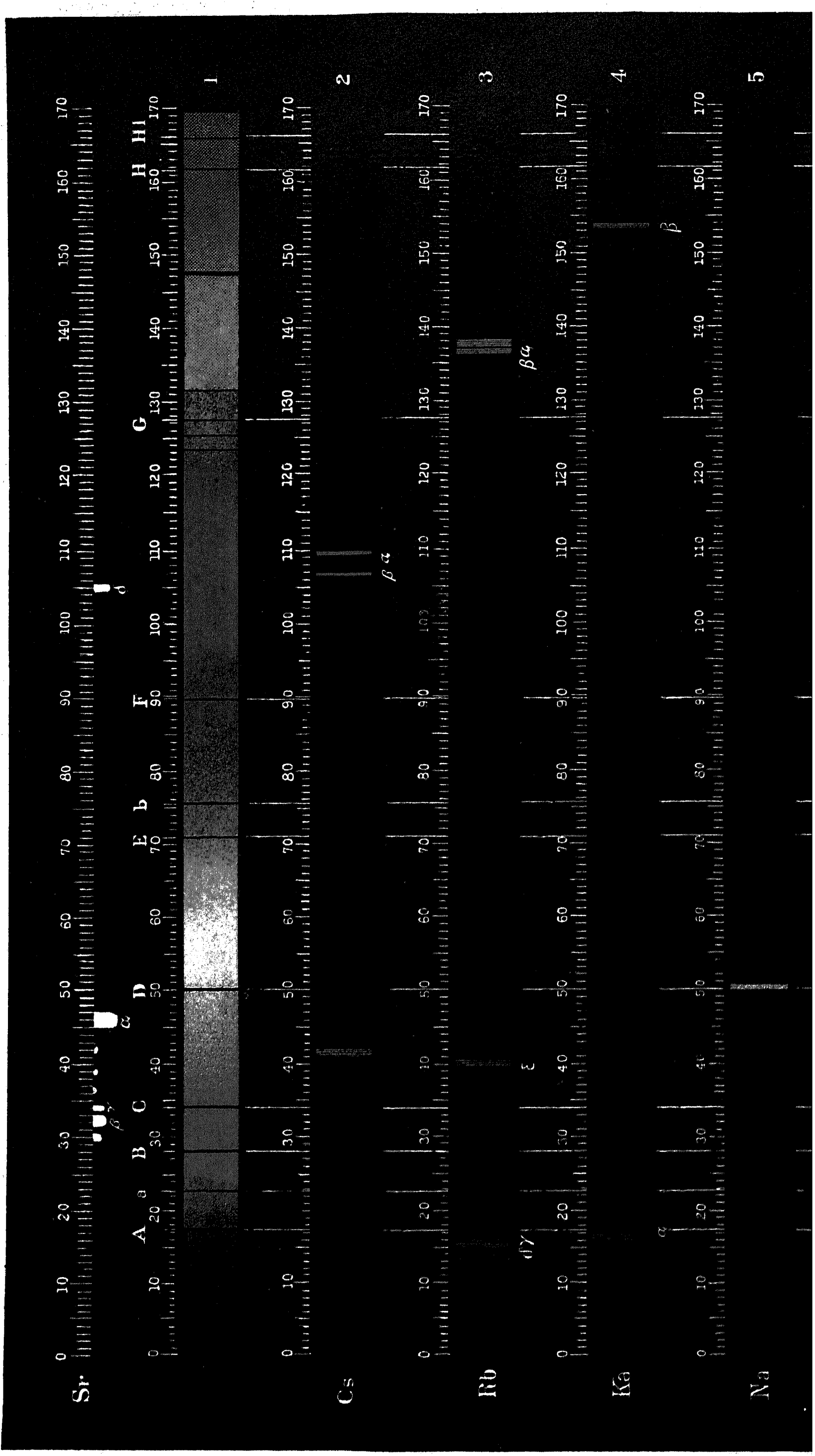
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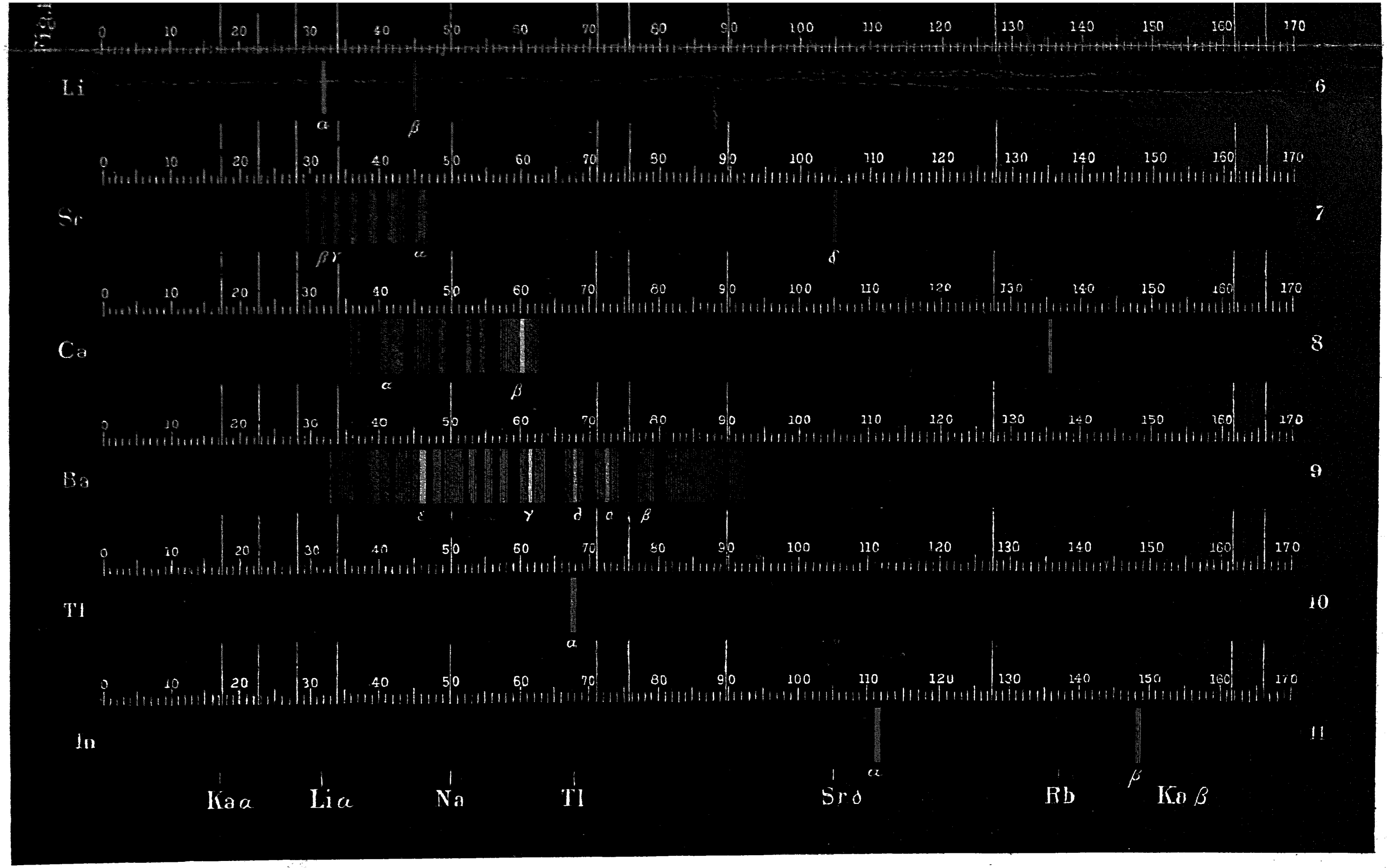
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INTRODUCTION

TO THE

RARER ELEMENTS.

BY

PHILIP E. BROWNING, PH.D.,
Assistant Professor of Chemistry, Kent Chemical Laboratory,
Yale University.

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FOURTH EDITION, THOROUGHLY REVISED.

SECOND IMPRESSION, CORRECTED

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PREFACE TO THE FOURTH EDITION.

In attempting to bring this work up to date for a new edition the author has made numerous changes and additions throughout.

The chapter on Radio-Elements has been thoroughly revised by Professor B. B. Boltwood, who contributed it originally to the second edition. Professor H. S. Uhler, who aided in the selection of certain spectroscopic material for the third edition, has furnished a plate showing the spectrum of gallium and also the spectra of certain gallium and indium products prepared in collaboration with the author. To both of these colleagues the author acknowledges his indebtedness.

The section dealing with the rare earths has been rearranged in accordance with recent researches in that field. The discovery of gallium, indium, and germanium in appreciable amounts in certain of our American commercial mineral products has furnished material for a wider study of these elements, and has made desirable a more extended description of their chemical behavior. The treatment of the subject of qualitative separation has been made fuller by the introduction of certain alternative methods; and some of the newer technical applications of the rarer elements have been noted. A table has been prepared to show the chief associates of these elements, and so to indicate the major analytical problems which face the chemist interested in them.

Special attention has been given to the revision of the experimental work, which now consists of about two hundred experiments. Included in these are adaptations, suitable for the laboratory, of processes by means of which compounds of practically all the rarer elements may be obtained from available minerals or from commercial by-products. A careful study of the experiments will accomplish the main purpose of the book.

The author wishes to reiterate the statement made in former prefaces that this little work is intended not to treat exhaustively the subject of the rarer elements, but rather to serve as an introduction to the study of an interesting group which the chemist in the inorganic field cannot afford to neglect.

NEW HAVEN, CONN., January, 1917.

PREFACE TO FIRST EDITION.

This small volume, prepared from material used by the author in a short lecture course given at Yale University, is intended to serve as a convenient handbook in the introductory study of the rarer elements; that is, of those elements which are not always taken up in a general course in chemistry. No attempt has been made to treat any part of the subject exhaustively, but enough references have been given to furnish a point of departure for the student who wishes to investigate for himself. Experimental work has been included except in the case of those elements which are unavailable, either because of their scarcity or because of the difficulty of isolating them.

The author has drawn freely upon chemical journals and standard general works. In his treatment of the rare earths he has made especial use of Herzfeld and Korn's *Chemie der seltenen Erden* and Truchot's *Les Terres Rares*, works which he gladly recommends. He gratefully acknowledges the valuable assistance of his wife in preparing this material for the press.

NEW HAVEN CONN., April, 1903.

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THE RARER ELEMENTS

CHAPTER I.

THE ALKALIES.

LITHIUM, Li, 6.94.

Discovery. In 1817 Arfvedson, working in Berzelius's laboratory upon a petalite from Uto, Sweden, discovered an alkali which he found to differ from those already known in the following particulars: (1) in the low fusing points of the chloride and sulphate; (2) in the hydroscopic character of the chloride; and (3) in the insolubility of the carbonate. In his analysis of the mineral it had remained associated with sodium, not being precipitated by tartaric acid. To the newly discovered element the name Lithium was given, from λίθος, *stone*, because it differed from sodium and potassium in having a mineral rather than a vegetable origin (Ann. der Phys. u. Chem. (1818), XXIX, 229; Ann. Chim. Phys. [2] X, 82). It has since been found, however, not only in the mineral kingdom, but in the vegetable and animal kingdoms also.

Occurrence. Lithium is found combined as follows:

(1) In minerals:

Petalite,	$LiAl(Si_2O_5)_2$,	contains	2–5%*	Li_2O.
Spodumene,†	$LiAl(SiO_3)_2$,	"	4–8%	"
Lepidolite,	$\overset{\text{I}}{R}_3Al(SiO_3)_3$,	"	4–6%	"
Zinnwaldite,	$(K,Li)_3FeAl_3Si_5O_{16}(OH,F)_2$,	"	3–4%	"
Cryolithionite,	$Li_3Na_3Al_2F_{12}$,	"	5–6%	Li

Cryophyllite, complex silicate, *vid.* Zinnwaldite, contains 4–5% Li_2O.

---

* In the tabulation of percentages the nearest whole numbers have generally been used in this book.

† The more important mineral sources are indicated by italics.

Irvingite, complex silicate, contains 4–5% Li_2O.
Polylithionite, complex silicates, *vid.* Zinnwaldite, contains about 9% Li_2O.

Beryl,	$Be_3Al_2(SiO_3)_6$,	contains	0–1%	**Li_2O.**
Triphylite,	$Li(Fe,Mn)PO_4$,	"	8–9%	"
Lithiophilite,	$Li(Mn,Fe)PO_4$,	"	8–9%	"
Amblygonite,	$Li(AlF)PO_4$,	"	8–10%	"
Natramblygonite,	$NaAl(OH)PO_4$,	"	3–4%	"

Sicklerite, $Fe_2O_3 \cdot 6MnO \cdot 4P_2O_5 \cdot 3(LiH)_2O$, cont's 3.8% Li_2O.

Small amounts of lithium are found also in some varieties of tourmaline, in epidote, muscovite, orthoclase, and psilomelane.

(2) In certain mineral waters, among which are Dürkheim, Kissingen, Baden-Baden, Bilin, Assmannshausen, Tarasp, Kreuznach, Salzschlirf, Aachen, Selters, Wildbad, Ems, Homburg, Karlsbad, Marienbad, Egger-Franzenbad, Wheal Clifford, Bad Orb, Sciacca, Salsomaggiore.

(3) In seaweed, tobacco, cacao, coffee, and sugarcane; in milk, human blood, and muscular tissue; in meteorites, soils,* and sea-water.

Extraction. Lithium may be extracted from minerals by the following methods:

(1) *From triphylite or lithiophilite.* The coarsely ground mineral is dissolved in hydrochloric acid to which nitric acid is gradually added, and the solution obtained is treated with a sufficient amount of ferric chloride to unite with all the phosphoric acid present. This solution is evaporated to dryness and the residue is extracted with hot water. The extract thus obtained is treated with barium sulphide, to remove the manganese and the last traces of iron. The barium is removed by sulphuric acid, and the filtrate is evaporated with oxalic acid and ignited. The alkalies remain as carbonates (Müller).

Lithium may be separated from the other alkalies by treating the mixed carbonates with water, lithium carbonate being comparatively insoluble.

(2) *From lepidolite (or any other silicate).* The mineral is

---

* *Vid.* Steinkoenig, J. Ind. Eng. Chem. VII, 425 (1915).

melted at red heat in a crucible, the melted mass is cooled rapidly in water and pulverized. Sufficient water is added to give the material the consistency of paste. Hydrochloric acid of specific gravity 1.2, equal in weight to the weight of the mineral taken, is gradually added, with stirring. The mass is allowed to stand for twenty-four hours. It is then heated again to about 100° C., with stirring, and a second portion of acid equal to the first is added. Upon several hours' heating the silica separates in the form of powder, and after treatment with nitric acid to oxidize the iron, the soluble material is separated by filtration from the silica. The filtrate is heated to the boiling-point and treated with sodium carbonate, which precipitates iron, aluminum, calcium, magnesium, manganese, etc. These are removed by filtration, and the liquid is evaporated to a small volume and filtered again if necessary. Lithium carbonate is precipitated by more sodium carbonate (Schrötter).

The Element. *A. Preparation.* Elementary lithium may be obtained (1) by subjecting the fused chloride or bromide to electrolysis; (2) by heating a mixture of elementary calcium and lithium chloride in the presence of hydrogen (Hackspill).

B. Properties. Lithium is a metallic element which has a silvery-white luster and which oxidizes in the air, though more slowly than potassium and sodium. It decomposes water at ordinary temperatures, and is light enough to float in petroleum. Its melting-point is 183° C.; its specific gravity is 0.59.

Compounds. *A. Typical forms.* The following are typical compounds of lithium:

Oxides, Li_2O; Li_2O_2. 85.45.
Hydroxide, LiOH.
Carbonate, Li_2CO_3.
Chloride, LiCl.
Chlorate, $LiClO_3 + 0.5H_2O$.

Perchlorate, $LiClO_4 + 3H_2O$.
Bromide, $LiBr$.
Bromate, $LiBrO_3$.
Iodide, $LiI + 3H_2O$.
Iodate, $LiIO_3 + 0.5H_2O$.
Periodate, $LiIO_4$.
Fluorides, LiF; $LiF \cdot HF$.
Nitride, LiN_3.
Nitrite, $LiNO_2 + 0.5H_2O$.
Nitrate, $LiNO_3$.
Sulphide, Li_2S.
Sulphite, Li_2SO_3.
Sulphates, Li_2SO_4; $KLiSO_4$; $NaLiSO_4$; etc.
Phosphates, LiH_2PO_4; $Li_3PO_4 + 0.5H_2O$; $Li_4P_2O_7$.
Carbide, Li_2C_2.
Silicofluoride, $Li_2SiF_6 + 2H_2O$.

B. *Characteristics.* Most of the salts of lithium are easily soluble in water; the principal exceptions are the carbonate, the phosphate, and the fluoride, which are difficultly soluble. Lithium resembles sodium more closely than it resembles the other alkalies, in that it does not form an insoluble chloroplatinate, nor a series of alums. The nitrate and the chloride are soluble in alcohol. The compounds of lithium color the flame brilliant crimson.

Estimation. Lithium is usually weighed as the sulphate or chloride.

Separation. Lithium may be separated from the other members of the alkali group (1) by the ready solubility of its chloride in amyl alcohol (Gooch, Amer. Chem. Jour. IX, 33); (2) by the solvent action of absolute ethyl alcohol upon the chloride;* (3) by the insolubility of the phosphate in the presence of ammonia and ethyl alcohol (Benedict, Amer.

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* At 25° C., 100 grm. ethyl alcohol dissolves amyl alcohol dissolves

	ethyl alcohol dissolves	amyl alcohol dissolves
LiCl............	25.8 grm.	9.03 grm.
NaCl............	0.065 "	0.002 "
KCl............	0.02 "	0.0008 "
RbCl............	0.078 "	0.0025 "

Chem. Jour. XXXII, 480); (4) by the comparative insolubility of the carbonate; (5) by the solubility of the fluosilicate (Reichard, Chem. Ztg. XXIX, 861); (6) by the solubility of the chloride in primary isobutyl alcohol (Winkler, Ztschr. f. anal. Chem. LII, 628); (7) by the solubility of the chloride in pyridine (Kahlenberg, Jour. Amer. Chem. Soc. XXIV, 401).

EXPERIMENTAL WORK ON LITHIUM.

Experiment 1. *Extraction of lithium salts from triphylite or lithiophilite.* Dissolve 25 to 50 grm. of finely powdered mineral in common hydrochloric acid, add sufficient nitric acid to oxidize the iron, and enough ferric chloride to combine with all the phosphoric acid present. Evaporate to dryness, and extract with hot water. Treat the extract with barium hydroxide in slight excess. Filter, add sulphuric acid to complete precipitation of barium sulphate, and filter again. Convert the sulphates present into carbonates by the careful addition of barium carbonate, filter, acidify the filtrate with hydrochloric acid, evaporate to dryness, and extract the lithium chloride with alcohol.

(Lithium salts may be extracted also from the mother-liquor after the extraction of cæsium and rubidium salts from lepidolite. The liquor is treated with barium carbonate in excess and is then boiled and filtered. The filtrate is acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol.)

Experiment 2. *Precipitation of lithium phosphate* (Li_3PO_4) *and lithium fluoride* (LiF). (*a*) To a solution of a lithium salt add sodium phosphate in solution. (*b*) Try similarly the action of sodium fluoride.

Experiment 3. *Precipitation of lithium carbonate* (Li_2CO_3). To a few drops of a concentrated solution of a lithium salt add sodium carbonate in solution.

Experiment 4. *Solvent action of alcohol upon lithium salts.* Try the action of ethyl or amyl alcohol upon a little dry lithium nitrate or chloride.

Experiment 5. *Flame and spectroscopic tests for lithium.* (*a*) Dip a platinum wire into a solution of a lithium salt and hold in a Bunsen flame. Note the color.

(*b*) Observe the lithium flame by means of the spectroscope. Note the bright crimson line between the potassium and sodium lines.

Experiment 6. *Negative tests of lithium salts.* Note that hydrogen sulphide, ammonium hydroxide, ammonium carbonate acting upon dilute solutions, chloroplatinic acid, and sodium cobaltic nitrite give no precipitate with lithium salts.

RUBIDIUM, Rb, 85.45.

Discovery. Rubidium was discovered by Bunsen and Kirchhoff in 1861, by means of the spectroscope, in the course of some work upon a lepidolite from Saxony (J. B. (1861), 173; Chem. News III, 357). The alkaline salts had been separated by the usual methods and precipitated with platinic chloride. The precipitate, when examined with the spectroscope, showed at first only the potassium lines. When it had been boiled repeatedly with water, however, the residue gave two violet lines situated between the strontium blue line and the potassium violet line at the extreme right of the spectrum. These increased in strength as the boiling continued, and with them appeared several other lines, among which were two almost coincident with the potassium red line (α) at the extreme left. These lines, observed for the first time, marked the discovery of an element; because of their color Bunsen gave it the name Rubidium, from the Latin *rubidus*, the deepest red.

Occurrence. Rubidium, like cæsium, is widely distributed, but in very small quantities. It is found

(1) In minerals:

Lepidolite,	$\overset{I}{R}_3Al(SiO_3)_3$,	contains	0.7–3.0%	Rb_2O.
Leucite,	$KAl(SiO_3)_2$,	"	traces	"
Spodumene,	$LiAl(SiO_3)_2$,	"	"	"
Triphylite,	$Li(Fe,Mn)PO_4$,	"	"	"
Lithiophilite,	$Li(Mn,Fe)PO_4$,	"	"	"
Carnallite,	$KMgCl_3 \cdot 6H_2O$,	"	"	"
Mica and orthoclase		contain	"	"
Some microclines		"	2.3	"

(2) In certain mineral waters, among which are the following: Ungemach, Ems, Kissingen, Nauheim, Selters, Vichy, Wildbad, Kochbrunnen (Wiesbaden), Dürkheim.

(3) In beet-root, many samples of tobacco, some coffee and tea, ash of oak and beech, crude cream of tartar, potashes, and mother-liquor from the Stassfurt potassium salt works.

Extraction. Rubidium may be extracted with cæsium from lepidolite (*vid.* Extraction of Cæsium).

The Element. *A. Preparation.* Elementary rubidium may be obtained (1) by heating the charred tartrates to a white heat (Bunsen); (2) by reducing the hydroxide or the carbonate with magnesium (Winkler, Ber. Dtsch. chem. Ges. XXIII, 51); (3) by reducing the hydroxide with aluminum (Beketoff); (4) by heating the chloride with calcium (*vid.* Lithium).

B. Properties. Rubidium is a soft white metal which melts at 38° C. It takes fire in the air, burning to the oxide. It decomposes water. Its specific gravity is 1.52.

Compounds. *A. Typical forms.* The following are typical compounds of rubidium:

Oxides, Rb_2O; Rb_2O_2; Rb_2O_3; Rb_2O_4.
Hydroxide, RbOH.
Carbonates, Rb_2CO_3; $RbHCO_3$.
Chloride, RbCl.
Double chlorides, $HgCl_2 \cdot 2RbCl$; $2PbCl_2 \cdot RbCl$; $BiCl_3 \cdot 6RbCl$;

$CdCl_2 \cdot 2RbCl$; $2AsCl_3 \cdot 3RbCl$; $3SbCl_3 \cdot 5RbCl$; $MnCl_2 \cdot 2RbCl + 2H_2O$; $ZnCl_2 \cdot 2RbCl$; $MgCl_2 \cdot RbCl + 6H_2O$; $AuCl_3 \cdot RbCl$; $TeCl_4 \cdot 2RbCl$; $TlCl_3 \cdot 2RbCl + H_2O$; and many others.

Chlorate, $RbClO_3$.

Perchlorate, $RbClO_4$.

Bromides, $RbBr$; $RbBr_3$.

Double bromides, $2PbBr_2 \cdot RbBr$; $2AsBr_3 \cdot 3RbBr$; $2SbBr_3 \cdot 3RbBr$; $AuBr_3 \cdot RbBr$; $TeBr_4 \cdot 2RbBr$; $TlBr_3 \cdot 3RbBr + H_2O$.

Iodides, RbI; RbI_3; and others.

Double iodides, $AgI \cdot 2RbI$; $PbI_2 \cdot RbI + 2H_2O$; $2AsI_3 \cdot 3RbI$; $2SbI_3 \cdot 3RbI$; $TeI_4 \cdot 2RbI$; $TlI_3 \cdot RbI + 2H_2O$.

Iodates, $RbIO_3$; $RbIO_3 \cdot HIO_3$; $RbIO_3 \cdot 2HIO_3$.

Nitride, RbN_3.

Nitrates, $RbNO_3$; $3RbNO_3 \cdot Co(NO_3)_3 + H_2O$.

Cyanide, $RbCN$.

Sulphates, Rb_2SO_4; $RbHSO_4$; $Rb_2S_2O_7$; $Rb_2O \cdot 8SO_3$.

Alums, $RbAl(SO_4)_2 + 12H_2O$; $RbFe(SO_4)_2 + 12H_2O$; $RbCr(SO_4)_2 + 12H_2O$; $Rb_2SO_4 \cdot Ti_2O_3 \cdot 3SO_3 + 24H_2O$.

Chloroplatinate, Rb_2PtCl_6.

Silicofluoride, Rb_2SiF_6.

B. Characteristics. The rubidium compounds are soluble, and similar to those of potassium and cæsium (*vid.* Cæsium). Among the important insoluble salts are the perchlorate ($RbClO_4$), the silicofluoride (Rb_2SiF_6), the chloroplatinate (Rb_2PtCl_6), the bitartrate ($RbHO_2C_4H_4O_4$), the alums ($RbAl(SO_4)_2+12H_2O$ and $RbFe(SO_4)_2+12H_2O$), and the cobaltic nitrite ($Rb_3Co(NO_2)_6$, typical). The salts of rubidium color the flame violet. The spectrum gives two lines in the violet to the right of the cæsium lines ($Rb\alpha$ and $Rb\beta$), also two lines not so distinct in the dark red ($Rb\gamma$ and $Rb\delta$), near the potassium red line, at the left of the spectrum.

Estimation, Separation, and Experimental Work. *Vid.* Cæsium.

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CÆSIUM, Cs, 132.81.

Discovery. Cæsium was discovered in 1860 by Bunsen and Kirchhoff while they were engaged in the spectroscopic examination of a mother-liquor from the waters of Dürkheim spring (Pogg. Annal. CXIII, 337; Chem. News II, 281). After the removal of the strontium, calcium, and magnesium, by well-known methods, and of the lithium as far as possible by ammonium carbonate, the mother-liquor was tested, and gave, in addition to the potassium, sodium, and lithium lines, two beautiful blue lines never before observed, near the strontium blue lines. Bunsen gave the name Cæsium to the newly discovered element, from the Latin *caesius*, the blue of the clear sky.

Occurrence. Cæsium is found in combination as follows:

(1) In minerals:

Pollucite, $H_2Cs_4Al_4(SiO_3)_9$, contains 31–37% Cs_2O.

Lepidolite, $LiK(Al(OH,F)_2)\cdot Al(SiO_3)_3$, contains 0.2–0.7% Cs_2O.

Beryl, $Be_3Al_2(SiO_3)_6$, contains 0–3% Cs_2O.

(2) In certain mineral waters, among which are Dürkheim (1 liter contains about 0.21 mg. RbCl and 0.17 mg. CsCl), Nauheim, Baden-Baden, Frankenhausen, Kreuznacher, Bourbonne les Bains, Monte Catino, Wheal Clifford.

(3) In ash from some tobacco.

Extraction. Of the methods in use for the extraction of cæsium the following may serve as examples:

(1) From *pollucite*. The finely powdered mineral is decomposed on a water-bath with strong hydrochloric acid, and the acid solution is treated in one of three ways: (*a*) with antimony trichloride, which precipitates the double chloride of antimony and cæsium ($3CsCl\cdot 2SbCl_3$) (Wells, Amer. Chem. Jour. XXVI, 265); (*b*) with a solution of lead chloride containing free chlorine, which precipitates a double chloride of cæsium and tetravalent lead ($2CsCl\cdot$

$PbCl_4$) (Wells, Amer. Jour. Sci. [3] XLVI, 186); (*c*) with an excess of ammonium alum crystals, the liquid being then allowed to crystallize, and cæsium alum coming down first ($CsAl(SO_4)_2 \cdot 12H_2O$) (Browning and Spencer, Amer. Jour. Sci. XLII, (1916), 279).

(2) *From any silicate.* The mineral is heated with a mixture of calcium carbonate and ammonium chloride, and the fused mass is cooled and extracted with water. The liquid is then evaporated to a small volume, and sulphuric acid is added to precipitate the calcium as the sulphate. After filtration, evaporation is continued until the greater part of the hydrochloric acid has been expelled. Sodium or ammonium carbonate is then added to complete the removal of the calcium salt. Upon the addition of chloroplatinic acid the cæsium and rubidium are precipitated as the salts of that acid. By the action of hydrogen upon these salts the platinum is precipitated, while the cæsium and rubidium chlorides are left in solution.

(3) *From lepidolite.* The mineral is decomposed by heating with a mixture of calcium fluoride and sulphuric acid (*vid.* Experiment 1).

The Element. *A. Preparation.* Elementary cæsium may be obtained (1) by heating cæsium hydroxide with aluminum to redness in a nickel retort (Beketoff, Bull. Acad. Petersburg IV, 247); (2) by heating cæsium hydroxide with magnesium in a current of hydrogen (Erdmann and Menke, Jour. Amer. Chem. Soc. XXI, 259, 420); (3) by heating cæsium carbonate with magnesium in a current of hydrogen (Graefe and Eckardt, Zeitsch. anorg. Chem. XXII, 158); (4) by heating the chloride with calcium (*vid.* Lithium).

B. Properties. Cæsium, the most positive of the metals, is silvery white and soft. It takes fire quickly in the air, burning to the oxide. It melts at 26° C. Like the other alkaline metals it decomposes water. Determinations of its specific gravity range from 1.88 to 2.4.

Compounds. *A. Typical forms.* The following are typical compounds of cæsium:

Oxides, Cs_2O; Cs_2O_2; Cs_2O_3; Cs_2O_4.

Hydroxide, $CsOH$.

Carbonates, Cs_2CO_3; $CsHCO_3$.

Chloride, $CsCl$.

Double chlorides, $AgCl \cdot CsCl$; $HgCl_2 \cdot CsCl$; $PbCl_4 \cdot 2CsCl$; $PbCl_2 \cdot 4CsCl$; $2BiCl_3 \cdot 3CsCl$; $CuCl_2 \cdot 2CsCl$; $Cu_2Cl_2 \cdot CsCl$; $CdCl_2 \cdot 2CsCl$; $2AsCl_3 \cdot 3CsCl$; $2SbCl_3 \cdot 3CsCl$; $SnCl_2 \cdot CsCl$; $Fe_2Cl_6 \cdot 6CsCl$; $CoCl_2 \cdot 3CsCl$; $NiCl_2 \cdot 2CsCl$; $MnCl_2 \cdot 2CsCl$; $ZnCl_2 \cdot 3CsCl$; $MgCl_2 \cdot CsCl + 6H_2O$; $AuCl_3 \cdot CsCl$; $PtCl_4 \cdot 2CsCl$; $PtCl_2 \cdot 2CsCl$; $PdCl_2 \cdot 2CsCl$; $TeCl_4 \cdot 2CsCl$; $TlCl_3 \cdot 3CsCl + H_2O$; and many others.

Bromides, $CsBr$; $CsBr_3$; $CsBr_5$.

Double bromides, $HgBr_2 \cdot CsBr$; $PbBr_2 \cdot 4CsBr$; $CuBr_2 \cdot 2CsBr$; $CdBr_2 \cdot 3CsBr$; $2AsBr_3 \cdot 3CsBr$; $CoBr_2 \cdot 2CsBr$; $NiBr_2 \cdot CsBr$; $ZnBr_2 \cdot 2CsBr$; $MgBr_2 \cdot CsBr + 6H_2O$; $AuBr_3 \cdot CsBr$; $TeBr_4 \cdot 2CsBr$; $2TlBr_3 \cdot 3CsBr$; and many others.

Iodides, CsI; CsI_3; CsI_5.

Double iodides, $HgI_2 \cdot CsI$; $PbI_2 \cdot CsI$; $CdI_2 \cdot 3CsI$; $2AsI_3 \cdot 3CsI$; $CoI_2 \cdot 2CsI$; $ZnI_2 \cdot 3CsI$; $TeI_4 \cdot 2CsI$; $TlI_3 \cdot CsI$; and many others.

Mixed halides, $HgCs_3Cl_3Br_2$; $HgCs_2Cl_2Br_2$; $HgCsClBr_2$; $Hg_5CsClBr_{10}$; $HgCs_3Br_3I_2$; $HgCs_2Br_2I_2$; $HgCsBrI_2$; $HgCs_2Cl_2I_2$; $PbCs_4(ClBr)_6$; $PbCs(ClBr)_3$; $Pb_2Cs(ClBr)_5$.

Double fluorides, $2CsF \cdot ZrF_4$; $CsF \cdot ZrF_4 + H_2O$; $2CsF \cdot 3ZrF_4 + 2H_2O$.

Iodates, $CsIO_3$; $2CsIO_3 \cdot I_2O_5$; $2CsIO_3 \cdot I_2O_5 + 2HIO_3$.

Nitride, CsN_3 (Jour. Amer. Chem. Soc. xx, 225).

Nitrates, $CsNO_3$; $3CsNO_3 \cdot Co(NO_3)_3 + H_2O$.

Sulphates, Cs_2SO_4; $CsHSO_4$; $Cs_2S_2O_7$; $Cs_2O \cdot 8SO_3$.

Alums, $CsAl(SO_4)_2 + 12H_2O$; $Cs_2SO_4 \cdot Mn_2(SO_4)_3 + 24H_2O$; $Cs_2SO_4 \cdot Ti_2O_3 \cdot 3SO_3 + 24H_2O$.

Fluosilicate, Cs_2SiF_6.

Chromates, Cs_2CrO_4; $Cs_2Cr_2O_7$.
Chloroplatinate, Cs_2PtCl_6.
Cobaltic nitrite, $Cs_3Co(NO_2)_6$,* typical.

B. Characteristics. With few exceptions the cæsium compounds are soluble in water. They closely resemble the potassium and rubidium compounds, being for the most part isomorphous with them. A comparison of the solubilities of the alums and also of the chloroplatinates of the three elements, at a temperature of 15°–17° C., follows:

100 parts of water will dissolve

$CsAl(SO_4)_2 + 12H_2O$,	0.62 parts;	Cs_2PtCl_6,	0.18 parts.
$RbAl(SO_4)_2 + 12H_2O$,	2.30 "	Rb_2PtCl_6,	0.20 "
$KAl(SO_4)_2 + 12H_2O$,	13.50 "	K_2PtCl_6,	2.17 "

Among the important insoluble salts are the chloroplatinate (Cs_2PtCl_6), the alum ($CsAl(SO_4)_2 + 12H_2O$), the cobaltic nitrite ($Cs_3Co(NO_2)_6$, typical), and the double chlorides with tetravalent lead ($PbCl_4 \cdot 2CsCl$), tetravalent tin ($2CsCl \cdot SnCl_4$?), and trivalent antimony ($3CsCl \cdot 2SbCl_3$). The salts of cæsium color the flame violet. The spectrum shows two sharply defined lines in the blue, designated on the scale as $Cs\alpha$ and $Cs\beta$.

Estimation of Cæsium and Rubidium. Cæsium and rubidium may be estimated in general by the methods applied to potassium. They are usually weighed as the normal sulphates, after evaporation of suitable salts with sulphuric acid and ignition of the products; other methods, however, such as the chloroplatinate and chloride methods, are possible. They may be weighed with a fair degree of accuracy as the acid sulphates, after evaporation with an excess of sulphuric acid, and heating at 250°–270° C. until a constant weight is obtained (Browning, Amer. Jour. Sci. [4] XII, 301). They may also be estimated by precipitation with sodium cobaltic nitrite, decomposition of the cobaltic nitrites with hydrochloric acid, and precipitation of the perchlorates by a 30% perchloric acid solution* (Montemartini, Gaz. chim. ital. XXXIII (II), 189; Chem. Zentr. 1904 (I), 119). Rubidium may be estimated by means of the spectroscope by comparing the intensity of the spectrum lines obtained from a definite amount of solution of rubidium salt to be estimated with that of the lines obtained from a definite amount of a solution of known strength (Gooch and Phinney, Amer. Jour. Sci. [3] XLIV, 392).

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* Cs may be partly replaced by Na.

Separation of Cæsium and Rubidium. These metals belong to the alkali group. From sodium and lithium they may be separated (1) by chloroplatinic acid, with which they form insoluble salts; and (2) by aluminum sulphate, with which they form difficultly soluble alums. From potassium they may be separated by the greater solubility of the potassium alum and chloroplatinate in water.

Cæsium and rubidium may be separated from each other (1) by the difference in solubility of the chloroplatinates;* (2) by the difference in solubility of the alums;† (3) by the formation of the more stable and less soluble tartrate of rubidium; and (4) by the solubility of cæsium carbonate in absolute alcohol. Probably the most satisfactory methods, however, are those suggested by Wells; they depend upon the insolubility of the following salts: cæsium double chloride and iodide ($CsCl_2I$) (Amer. Jour. Sci. [3] XLIII, 17), cæsium-lead chloride (Cs_2PbCl_6) (ibid. [3] XLVI, 186), and cæsium-antimony chloride ($Cs_3Sb_2Cl_9$) (Amer. Chem. Jour. XXVI, 265).

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* *Vid.* also Gooch and Blake (Amer. Jour. Sci. [4] XLIV, 381).

† *Vid.* p. 12.

EXPERIMENTAL WORK ON CÆSIUM AND RUBIDIUM.

Experiment 1. *Extraction of cæsium and rubidium salts from lepidolite.* Mix thoroughly in a lead or platinum dish 100 grm. of finely ground lepidolite with an equal amount of powdered fluorspar. Add 50 cm.^{3} of common sulphuric acid and stir until the mass has the consistency of a thin paste. Set aside in a draught hood until the first evolution of fumes (SiF_4 and HF) has nearly ceased. Heat on a plate or sand-bath at a temperature of 200°–300° C. until the mass is dry and hard. Pulverize and extract with hot water until the washings give no precipitate on the addition of ammonium hydroxide to a few drops. Evaporate the entire solution to about 100 cm.^{3} and filter while hot to remove the calcium sulphate. Set the clear filtrate aside to crystallize.* The crystals, consisting of a mixture of potassium, cæsium, and rubidium alums, with some lithium salt, should be dissolved in about 100 cm.^{3} of distilled water, and allowed to recrystallize. This process of recrystallization should be repeated until the crystals give no test before the spectroscope for either lithium or potassium. The amount of cæsium and rubidium alums obtained will of course vary with the variety of lepidolite used. An average amount of the mixed alums of potassium, cæsium, and rubidium from the first crystallization would be 10 grm. The pure cæsium and rubidium alums finally obtained should be about 3 grm. (Robinson and Hutchins, Amer. Chem. Jour. VI, 74). Lithium may be extracted from the mother-liquor (*vid.* Experiment 1, Lithium).

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* If this solution is evaporated to a small volume and saturated with $NH_4Al(SO_4)_2 \cdot 12H_2O$ the crystallization of the Cs and Rb alums will be facilitated (Browning and Spencer).

Experiment 2. *Preparation of cæsium and rubidium sulphates* (Cs_2SO_4; Rb_2SO_4). Dissolve in water a crystal of the cæsium and rubidium alums obtained from lepidolite, add a few drops of ammonium hydroxide, and boil. Filter off the aluminum hydroxide and evaporate the filtrate to dryness. Ignite until the ammonium sulphate is removed, dissolve in a few drops of water, filter, and evaporate to dryness. Sulphates of cæsium and rubidium will remain.

Experiment 3. *Preparation of the carbonates of cæsium and rubidium* (Cs_2CO_3; Rb_2CO_3). Dissolve in water a crystal of cæsium and rubidium alums obtained from lepidolite, add an excess of barium carbonate, and boil. Filter off the alumina, barium sulphate, and excess of barium carbonate. Pass a little carbon dioxide through the clear filtrate and boil to remove traces of barium salt. Filter. Carbonates of cæsium and rubidium will remain in solution.

Experiment 4. *Formation of the double chloride of cæsium and tetravalent lead* ($2CsCl \cdot PbCl_4$). To a few cm.^{3} of a one per cent. solution of a cæsium salt add a few drops of the reagent obtained by warming lead dioxide with hydrochloric acid and allowing the solution to stand until cool. Make a similar experiment, using a rubidium salt in place of the cæsium salt. Note the absence of precipitation in this case.

Experiment 5. *Precipitation of the double chloride of cæsium and antimony* ($3CsCl \cdot 2SbCl_3$). To a few cm.^{3} of a one per cent. solution of a cæsium salt add some antimony trichloride in solution and evaporate to a small volume. The double chloride will be precipitated on cooling. Repeat the experiment, using a rubidium salt. Note the absence of precipitation in this case.

Experiment 6. *Precipitation of the double salt cæsium chloride and stannic chloride* ($2CsCl \cdot SnCl_4$). Make an experiment similar to Experiment 5, using stannic chloride in the place of antimonious chloride. Note the separation of the double chloride on cooling. Make a similar experiment, using a rubidium salt.

Experiment 7. *Precipitation of the chloroplatinates of cæsium and rubidium* (Cs_2PtCl_6; Rb_2PtCl_6). To a few cm.^{3} of a solution of a cæsium salt add a few drops of a solution of chloroplatinic acid. Make a similar experiment with a solution of a rubidium salt.

Experiment 8. *Precipitation of the cobaltic nitrites of cæsium and rubidium.* Try the action of a solution of sodium cobaltic nitrite upon separate solutions of cæsium and rubidium salts.

Experiment 9. *Precipitation of the alums of cæsium and rubidium.* To a few drops of a concentrated solution of a cæsium salt add about 5 cm.^{3} of a saturated solution of ammonium alum. Note the precipitation of the cæsium alum. Make a similar experiment with a rubidium salt.

Experiment 10. *Flame tests for cæsium and rubidium.* Dip the end of a platinum wire into a solution of a cæsium salt and test the action of the flame of a Bunsen burner upon it. Repeat, using a rubidium salt.

Experiment 11. *Spectroscopic tests for cæsium and rubidium.* Test solutions of cæsium and rubidium salts before the spectroscope. Note the twin blue lines of the cæsium spectrum and the twin violet lines of the rubidium.

Experiment 12. *Negative tests of cæsium and rubidium.* Note that hydrogen sulphide, ammonium sulphide, and ammonium carbonate give no precipitates with salts of cæsium and rubidium.

CHAPTER II.

BERYLLIUM, Be, 9.1.

Discovery. In the year 1797, Vauquelin discovered beryllium or glucinum in the mineral beryl (Ann. de Chim. XXVI, 155). After having removed the silica in the usual manner, he precipitated with carbonate of potassium, and treated the precipitate with a solution of caustic potash. The greater part of the precipitate dissolved, but the presence of something other than alumina was shown by precipitation when the solution was boiled. The new precipitate, dissolved in sulphuric acid, gave on evaporation irregular crystals having a sweetish taste and forming no alum with potassium sulphate. In his early articles Vauquelin refers to the oxide as "la terre du Béril," which the German chemists translated, "Berylerde." The sweet taste suggested for the new element the name Glucinum, from γλυκύς, *sweet*. The name Beryllium, from the chief source, beryl, has been more generally used.

Occurrence. Beryllium occurs in minerals as follows:

Beryl,	$Be_3Al_2(SiO_3)_6$,	contains	11–15%	BeO.
Chrysoberyl,	$BeAl_2O_4$,	"	19–20%	"
Bertrandite,	$Be_2(Be \cdot OH)_2Si_2O_7$,	"	40–43%	"
Phenacite,	Be_2SiO_4,	"	44–46%	"
Leucophanite,	$Na(BeF)Ca(SiO_3)_2$,	"	10–12%	"
Meliphanite,	$NaCa_2Be_2FSi_3O_{10}$	"	10–14%	"
Epididymite,	$HNaBeSi_3O_8$,	"	10–11%	"
Euclase,	$Be(Al \cdot OH)SiO_4$,	"	17–18%	"
Helvite or *danalite,*	$\overset{II}{R}_5(\overset{II}{R}_2S)(SiO_4)_3$,	"	13–14%	"

Gadolinite,	$FeBe_2Y_2Si_2O_{10}$,	contains	5–11%	BeO.
Trimerite,	$Be(Mn,Ca,Fe)SiO_4$,	"	16–17%	"
Cyrtolite,	complex silicate,	"	14–15%	"
Alvite,	" "	"	circa 14%	"
Allanite,	" "	"	0–.3%	"
Muromonite,	" "	"	5–6%	"
Erdmanite,	" "	"	0–4%	"
Foresite,	" "	"	0–1%	"
Arrhenite,	complex silico-tantalate,	"	circa 1%	"
Beryllionite,	$NaBePO_4$,	"	19–20%	"
Herderite,	$Ca(Be(OH,F))PO_4$,	"	15–16%	"
Hambergite,	$Be(BeOH)BO_3$,	"	53–54%	"
Sipylite,	$ErNbO_4$.	"	circa .6%	"
Tengerite,	complex carbonate,	"	9–10%	"

Beryllium is found also in traces in some monazite sands and aluminous schists, and in some mineral waters.

Extraction. Beryllium is generally extracted from beryl by one of the following methods:

(1) The mineral is fused with sodium or potassium hydroxide (*vid.* Experiment 1).

(2) The finely ground mineral is fused with three times its weight of potassium fluoride. The fused mass is treated with strong sulphuric acid and warmed; by this process the silica is removed as silicon fluoride, and the alumina and potash are united to form the alum, which may be crystallized out on evaporation. The beryllium remains in solution as the sulphate, and may be removed by the treatment described in Experiment 1.

(3) The mineral is fused with calcium fluoride. This process is in general the same as the one indicated in the second method, except that calcium sulphate is formed and must be removed (Lebeau, Chem. News LXXIII, 3).

(4) The mineral is decomposed by fusion (*a*) with

sodium and potassium carbonates, or (*b*) with acid potassium sulphate.

The Element.* *A. Preparation.* Elementary beryllium may be obtained (1) by bringing together the vapor of the chloride and sodium in a current of hydrogen (Debray, Ann. Chim. Phys. (1855) XLIV, 5); (2) by fusing the chloride with potassium (Wöhler, Pogg. Annal. XIII, 577); (3) by heating the chloride in a closed iron crucible with sodium (Nilson and Pettersson, Ber. Dtsch. chem. Ges. XI, 381, 906); (4) by electrolyzing the double fluoride of beryllium and sodium or potassium (Lebeau); (5) by heating the chloride in a bomb with sodium (Hunter).

B. Properties. The element beryllium is dark steel-gray in color. At ordinary temperatures unchanged in air and in oxygen, it burns brightly to the oxide when heated in either. It does not decompose hot or cold water. When heated it combines readily with fluorine, chlorine, bromine and iodine. It is soluble in dilute and in concentrated acids; also in potassium hydroxide with the liberation of hydrogen. Determinations of its specific gravity range from 1.75 to 1.85.

Alloys of beryllium with many of the common metals are known, as are also alloys with chromium, molybdenum and tungsten (Lebeau). An alloy of copper and beryllium containing from .5% to 1.3% beryllium is very sonorous.

Compounds. *A. Typical forms.* The following are typical compounds of beryllium:

Fluorides, BeF_2; $BeF_2.2NaF$; $BeF_2.2KF$; $BeF_2.2NH_4F$.
Chlorides, $BeCl_2$; $BeCl_2.AuCl_3$; $BeCl_2.FeCl_3.H_2O$; $BeCl_2.CrCl_3.H_2O$; $3BeCl_2.Tl_2Cl_6$; $BeCl_2.2ICl_3.8H_2O$; $BeCl_2.PtCl_2.5H_2O$; $BeCl_2.PtCl_4.8H_2O$; $BeCl_2.PdCl_2.6H_2O$; $BeCl_2.PdCl_4.8H_2O$.
Bromide, $BeBr_2$.
Iodide, BeI_2.

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* *Vid.* also Fichter and Jablczynski, Ber. dtsch. chem. Ges. XLVI, 1604.

Hydroxide, $Be(OH)_2$.
Oxide, BeO.
Sulphide, BeS.
Cyanides, $BePt(CN)_4.4H_2O$; $BeMg_2Pt_3(CN)_{12}$; $BePtBr_2(CN)_4$.
Carbides, Be_2C; $3Be_2C.B_6C$.
Nitride, Be_3N_2.
Sulphates, $BeSO_4$; $BeSO_4.2H_2O$; $BeSO_4.4H_2O$; $BeSO_4.K_2SO_4.2H_2O$; $BeSO_4.K_2SO_4.KHSO_4.4H_2O$; $3BeSO_4.2Na_2SO_4.12H_2O$; $BeSO_4.(NH_4)_2SO_4.2H_2O$.
Sulphites, $BeSO_3.H_2O$; $BeSO_3.2H_2O$; $2BeSO_3.K_2SO_3.9H_2O$; $2BeSO_3.(NH_4)_2SO_3.4H_2O$.
Selenate, $BeSeO_4.4H_2O$.
Selenites, $BeSeO_3.H_2O$; $BeSeO_3.2H_2O$.
Nitrate, $Be(NO_3)_2.4H_2O$.
Phosphates, $BeHPO_4.3H_2O$; $BeKPO_4$; $BeNaPO_4$; $BeNa_2(NH_4)_2(PO_4)_2$.
Antimonate, $Be(SbO_3)_2.6H_2O$.
Carbonate, $xBeCO_3.yBe(OH)_2$.
Silicates, $BeSiO_3$; $Be_3Al_2(SiO_3)_6$.
Aluminate, $Be(AlO_2)_2$.
Methyl, $Be(CH_3)_2$.
Ethyl, $Be(C_2H_5)_2$.
Propyl, $Be(C_3H_7)_2$.
Acetates, $Be(C_2H_3O_2)_2$; $Be_4O(C_2H_3O_2)_6$.
Acetylacetonate, $Be(C_5H_7O_2)_2$.
Oxalates, $BeC_2O_4.3H_2O$; $BeC_2O_4.K_2C_2O_4$; etc.
Tartrates, $BeC_4H_4O_6.3H_2O$; $KBeC_4H_3O_6$; $K_2Be_4C_8H_4O_{13}.7H_2O$; $Na_2Be_4C_8H_4O_{13}.10H_2O$.
and many salts of organic acids; e. g., succinates, racemates, malates, formates, propionates, butyrates, trichloracetate (Parsons and Sargent, Jour. Amer. Chem. Soc. XXXI, 1202).

B. Characteristics. The compounds of beryllium closely resemble those of aluminum. The oxide is white; it is insoluble in water and unaffected by it. The hydroxide is soluble in concentrated solutions of its own salts and is precipitated from them by dilution. It is also soluble in the alkali hydroxides and bicarbonates, and in dilute acids. The halides are very readily hydrolyzed by water, the hydrolysis in the case of the chlorides, bromides, and iodides being practically complete. Normal salts of the non-volatile acids only can be crystallized from water; of these the sulphate, oxalate, and selenate are examples. The nitrate can be prepared only by crystallization from strong nitric acid.

The double alkali tartrates are of peculiar interest, both on account of the fact that beryllium appears to replace not only the positive hydrogen of the acid but also in part the hydrogen of the tartrate ion, and also because the presence of beryllium in the salt increases the molecular rotation. This influence upon the molecular rotation is shown to an even greater degree in the case of the malates (Rosenheim and Itsig). Another interesting compound is the basic acetate, which, although almost insoluble in water, becomes soluble after hydrolysis by hot or cold water. It is soluble without decomposition in glacial acetic acid, methyl, ethyl, and amyl alcohols, chloroform, turpentine, ether acetone, carbon disulphide, and some other organic solvents. It is unaffected by dry air, melts at 283°–284° C., boils at 330°–331° C., and may be sublimed. It was used by Parsons in determining the atomic weight of beryllium. It is best prepared by the action of glacial acetic acid upon the dry carbonate or hydroxide. The chloride, nitrate and sulphate are the common soluble salts, and the nitrate and chloride are soluble in alcohol.

The arc spectrum of beryllium is characterized by lines in the blue and indigo.

Estimation. Beryllium is ordinarily estimated as the oxide, (BeO), which is obtained by the ignition of the precipitated hydroxide.

Separation. Beryllium closely resembles aluminum in many reactions. It may be separated from aluminum (1) by the action of a saturated solution of acid sodium carbonate upon the hydroxides of iron, aluminum and beryllium, beryllium hydroxide being dissolved (Parsons and Barnes); (2) by saturation of a solution of the two chlorides with hydrochloric acid gas in the presence of ether, the beryllium remaining in solution, while the aluminum chloride is precipitated (Gooch and Havens, Amer. Jour. Sci. [4] II, 416); (3) by the action of hot glacial acetic acid upon the acetates, basic beryllium acetate separating out on cooling (Parsons and Robinson); (4) by dehydration of the nitrates with amyl alcohol, the beryllium nitrate dissolving (Browning and Kuzirian); (5) by heating the acetates, the beryllium acetate subliming (Kling and Gelin, Bull. Soc. Chim. [4] XV, 205;) (6) by the action of acetyl chloride in acetone on the chlorides (Minnig, Amer. Jour. Sci. XL, 482).

EXPERIMENTAL WORK ON BERYLLIUM.

Experiment 1. *Extraction of beryllium salts from beryl* ($Be_3Al_2Si_6O_{18}$). Fuse in a nickel or iron crucible 10 grm. of finely powdered mineral with 10 grm. of potassium hydroxide, and cool. Pulverize the fused mass, add water enough to cover it, and strong sulphuric acid in slight excess. Heat the gelatinous mass until fumes of sulphuric acid are given off and the residue has the appearance of a fine white powder. Extract thoroughly with hot water, discarding the insoluble material. Evaporate until the alums begin to crystallize from the solution, and allow to stand, when the greater part of the aluminum will separate as the alum. Treat the mother liquor from the alum with nitric acid, to convert all iron present to the ferric condition, neutralize with ammonium hydroxide, and add sodium acid carbonate in crystals to saturation, warming gently (50° C.), with frequent stirring for about an hour; or, if the quantity of hydroxide is small, bring rapidly to boiling and boil for one minute only. Filter, add a little ammonium sulphide to remove any iron in solution, filter, and dilute with about five or ten volumes of water. Pass steam through the liquid, or boil if the amount of beryllium is small, to precipitate the basic carbonate of beryllium (Parsons).

Experiment 2. *Precipitation of beryllium hydroxide* ($Be(OH)_2$). (*a*) To a solution of a beryllium salt add ammonium hydroxide, and note the insolubility of the precipitate in excess of that reagent.

(*b*) To another portion of the beryllium solution add a solution of potassium or sodium hydroxide, and note the solvent action of an excess.

(*c*) Dilute with water a portion of the alkaline solution obtained in (*b*) and boil. Note the reprecipitation of the hydroxide.

(*d*) To another portion of the alkaline solution obtained in (*b*) add ammonium chloride, and boil.

(*e*) To a solution of a beryllium salt add ammonium sulphide.

Experiment 3. *Precipitation of basic beryllium carbonate* ($xBeCO_3.yBe(OH)_2$). (*a*) To a solution of a beryllium salt add sodium or potassium carbonate in solution. Note the solvent action of an excess and the reprecipitation on boiling.

(*b*) Make a similar experiment, using ammonium carbonate. Note solubility in excess.

Experiment 4. *Precipitation of beryllium phosphate* ($Be_3(PO_4)_2$). To a solution of a beryllium salt add a solution of sodium phosphate.

Experiment 5. *Preparation of beryllium basic acetate* ($Be_4O(C_2H_3O_2)_6$). Dissolve some beryllium hydroxide or carbonate in acetic acid and evaporate to dryness. Dissolve the dry residue in excess of hot glacial acetic acid and allow the solution to cool.

Experiment 6. *Action of sodium acid carbonate and of ammonium carbonate upon beryllium hydroxide.* (*a*) To a small amount of washed beryllium hydroxide add 2–3 grm.

of solid sodium acid carbonate and 20 cm.^{3} of water, and heat rapidly to boiling. Note the solubility of the hydroxide. Dilute to 200 cm.^{3} and boil. Note the precipitation of the hydroxide.

(*b*) Try similarly the action of ammonium carbonate, and note the solubility of the hydroxide in that reagent.

Experiment 7. *Solubility of beryllium salts in amyl alcohol.* To a few drops of a solution of beryllium chloride or nitrate add 5 cm.^{3} of amyl alcohol and bring to the boiling point of the alcohol. Note the solubility of the salts in the alcohol.

Experiment 8. *Negative tests of beryllium salts.* Try the action of hydrogen sulphide and ammonium oxalate upon separate portions of a solution of a beryllium salt. Add sodium acetate to a solution of a beryllium salt and boil. Note the absence of precipitation in each case.

CHAPTER III.

THE RADIO-ELEMENTS.*

THE property of matter known as radioactivity was discovered in 1896 by M. Henri Becquerel, who observed that the salts of uranium emitted a characteristic radiation which was capable of producing an effect on a photographic plate through several thicknesses of black paper wholly opaque to ordinary light.

The radiation emitted by radioactive substances has been shown to be complex in character and to include three distinctive types known as the α, β and γ radiations.

The α radiation consists of positively electrified atoms of helium moving with a velocity equal to about 1-15 of the velocity of light. The α rays are completely stopped by thin layers of ordinary matter and are deflected by strong magnetic and electrostatic fields.

The β radiation consists of negatively electrified particles having a mass about one eighteen-hundredth that of a hydrogen atom and projected at a velocity which in some cases is as high as nine-tenths the velocity of light. The β rays have a greater power for penetrating matter than the α rays, but are more readily deflected than the latter by both magnetic and electrostatic fields.

The γ radiation is believed to consist of ether pulses travelling with the velocity of light, and analogous in many respects to the Roentgen or X radiation. The γ rays have a high penetrative power and are not affected by either electrostatic or magnetic fields.

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* This chapter was contributed by Bertram B. Boltwood, Ph.D., of Yale University.

All three types of radiation are capable of producing charged carriers of electricity, known as ions, in the gases which they traverse, and in this manner render the gases conductive to electricity. They also excite phosphorescence in various chemical compounds and produce an effect on photographic plates.

The chemical elements which exhibit the phenomena of radioactivity are termed radio-elements. In order to explain their behavior, a theory, known as the disintegration theory, was proposed in 1902 by Rutherford and Soddy and has now been generally accepted. In this theory it is assumed that the radio-elements represent unstable forms of matter the atoms of which are spontaneously undergoing changes which result in the production of new forms of matter having different physical and chemical properties. These changes are accompanied by the emission of energy usually appearing in the form of heat derived from the internal energy of the atoms in process of transformation. The disintegration of the radio-elements takes place according to a simple exponential law which is given by the expression $N = N_0e^{-\lambda t}$, where N_0 is the number of atoms of the element present at the start, N is the number remaining unchanged after any time t, e is the base of the natural system of logarithms and λ is the constant of change of the given element. The constant of change is a definite and characteristic quantity for any particular radio-element and its value is unaffected by any of the extremes of temperature and pressure to which it has been possible to subject radioactive substances. The constant of change represents the fraction of any given quantity of the radio-element which undergoes transformation in the unit of time.

The disintegration of the radio-elements is wholly independent of the chemical state or form of combination of the radio-elements, and proceeds at a constant rate which is the same in all compounds of the same element. As a necessary consequence of this fact the relative radioactivity of different chemical compounds of the same radio-element is directly proportional to the relative quantities of the element which they each contain.

The instability of atomic structure may continue through a considerable number of successive changes until a final stable form of matter is reached. A radio-element from which any other radio-element is formed is called the ".parent" of the latter and the element formed is known as the "product" of the parent from which it is produced.

The known radio-elements can be divided into two general groups: the uranium series and the thorium series. The uranium series comprises uranium and twenty-three products of uranium, including ionium, radium, actinium, and polonium. The thorium series contains ten members in addition to thorium itself. The chemical behavior of the radio-elements, with the exception of uranium, radium, ionium, mesothorium, and thorium, has not been completely investigated, but there is every reason for believing that they all possess distinct and characteristic chemical properties.

THE RADIO-ELEMENTS AND THE PERIODIC TABLE.

The study of radioactivity has led to the discovery and identification of no less than thirty-three new and hitherto unsuspected elementary forms of matter or radio-elements. When the existence of the greater number of these had been recognized it appeared at first sight to be quite impossible to find any places for them in the Periodic Table. A position could be found for radium in Group II in the ninth horizontal row under barium, which corresponded satisfactorily to its atomic weight and chemical properties, but there appeared to be an insufficient number of vacant spaces to accommodate the greater number of other radio-elements. This obstacle was overcome by the recognition of the fact that the position of the various elements in the Periodic Table was determined by the value known as the *atomic number* of each element rather than by its atomic weight as had previously been assumed. The atomic number of an element is dependent on the electrical structure of the atom and can be determined directly by suitable experimental methods. Since the position of an element in the Periodic Table is established by its atomic number, and since the value of the atomic number is not directly dependent on the atomic weight, it is apparently possible for two elements to have different atomic weights and yet have identical atomic numbers, and therefore to occupy the same space in the Periodic Table. Further, since the chemical properties and probably also the spectra of the elements are dependent on the atomic numbers, it is possible for two different elements to have identical chemical properties and to show an identical spectrum. Such elements can be separately identified only by their different atomic weights or by means of some property which is independent of their chemical characteristics. The radioactive properties of the radio-elements offer such an independent means of identification. Radio-elements have been found which are absolutely inseparable chemically from other well-known inactive elements and many cases are recognized of radio-elements which are inseparable from other radio-elements. Elements which show this identity with other elements are called *isotopes* and their properties are said to be *isotopic*.

Through the application of the theory of isotopes and the calculation or determination of the atomic numbers of the radio-elements it has been possible to assign suitable positions to them in the last two rows of the Periodic Table. As a matter of fact the existence of the radio-elements has

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led to an extension of our knowledge and a better understanding of the significance of the periodic sequence of the elements.

URANIUM, U, 238.5.

The general properties of uranium will be discussed in Chapter VIII. It is one of the most slowly changing of the radio-elements, its rate of disintegration corresponding to the transformation in one year of about one eight-billionth of the total amount of uranium present. The time required for exactly one-half of any given quantity of uranium to disintegrate completely into other forms of matter is about five billion years. Ordinary uranium is supposed to consist of a mixture of two isotopic elements, uranium 1 with an atomic weight of 238 and uranium 2 with an atomic weight of 234. Uranium when completely freed from its disintegration products emits only α rays, but unless freshly prepared its compounds contain uranium X, which is the source of both a β and a γ radiation. Uranium salts can be obtained free from uranium X by recrystallization, the uranium X remaining in the mother liquor.

Uranium X. Uranium X is the first disintegration product of uranium and is gradually formed in uranium salts on standing. The amount which accumulates reaches a maximum after about 150 days, when a state of radioactive equilibrium is reached and the amount of uranium X which is produced in any subsequent time is exactly equal to the amount which disintegrates in the same period. Uranium X was first discovered by Crookes in 1900. It emits β and γ rays, and in 24 days one-half of any given quantity of it is transformed into other substances. It can be obtained free from uranium by treating pure uranium nitrate, dried at 118°, with ordinary ether. The uranium nitrate is dissolved by the ether, leaving a slight residue which contains the greater part of the uranium X. Uranium X is isotopic with thorium and when freshly prepared consists of a mix-

406

546.4
N19

ture of two isotopic elements, uranium X_1, and uranium X_2.

IONIUM, Io.

Ionium is a radio-element intermediate between uranium, of which it is a product, and radium, of which it is the parent. It was discovered by Boltwood in 1907. It has not been obtained pure in sufficient quantity to permit a determination of its atomic weight or of its spectrum, but atomic weight determinations on mixtures of ionium with thorium give good agreement with the theoretical assumption that its atomic weight is about 230. From uranium minerals containing thorium the ionium is separated with the thorium, with which it is isotopic. The constant of change of ionium has not yet been determined, but its rate of transformation is very possibly as slow as that of radium.

RADIUM, Ra, 226.5.

Discovery. Radium was discovered in 1898 by P. and S. Curie and G. Bemont. In the course of an investigation of the relative radioactivity of certain uranium salts and uranium minerals it was noted by Mme. Curie that although the activity of the uranium salts was quite closely proportional to the amounts of uranium contained in them, the activity of the uranium minerals was much greater than was to be expected from the uranium which they contained. This suggested that there might be present in the minerals some other more strongly radioactive constituent, and a further investigation led to the isolation of a highly radioactive substance resembling barium in its chemical properties.

Occurrence. Radium has been found widely distributed in minute proportions in many rocks and minerals, in sea water and in the waters of certain mineral springs. The chief source of radium has been the minerals containing a higher proportion of uranium, principally carnotite, and the present supply has been largely obtained from the carnotite ores of southwestern Colorado. One of the early sources of supply was the insoluble residues remaining after the treatment of pitchblende for the commercial extraction of uranium.

Extraction. From pitchblende residues. These consist chiefly of the sulphates of lead and calcium, together with the oxides of silicon, aluminum and iron. They also contain greater or less quantities of nearly all the metals (copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, the rare earths, niobium, tantalum, arsenic, barium, etc.). They are first treated with boiling, concentrated sodium hydroxide solution, washed with water, and digested with hydrochloric acid. Much of the material is removed in this operation, the radium remaining in the undissolved portion. After further washing, the residue is boiled with a concentrated sodium carbonate solution which converts the alkali-earths into carbonates. The residue is again washed to remove all traces of sulphates, and is then treated with hydrochloric acid, which dissolves the barium and radium together with certain of the other constituents. The solution of the chlorides is further purified until a salt containing only barium and radium is obtained. The mixed chlorides of barium and radium are subjected to a long series of fractional recrystallizations, the radium being concentrated in the least soluble portion of the fractions. In this manner a pure chloride of radium is ultimately obtained. The concentration of the radium proceeds more rapidly if the recrystallization is conducted with the double bromide.

From carnotite. The ore is decomposed by nitric acid, and barium chloride is added to the solution in the proportion of two pounds of barium chloride to one ton of ore. The radium barium sulphate is then precipitated by sulphuric acid and the sulphate is reduced with carbon to the sulphide. The sulphide is dissolved in hydrochloric acid and the radium barium chloride is subjected to fractional crystallization (Parsons, Moore, Lind and Schaefer, Bureau of Mines, Bull. 104, page 30 (1915)).

The Element. By the electrolysis of a solution of radium chloride with a mercury cathode, S. Curie and Debierne in 1910 obtained radium amalgam which on distillation in hydrogen left a residue of metallic radium. It is a white metal melting at about 700°. It alters rapidly in the air with the formation of nitride and decomposes water with the formation of the hydroxide.

Compounds. *A. Typical forms.* The following compounds of radium have been described:

Hydroxide, $Ra(OH)_2$.	Chloride, $RaCl_2$; $RaCl_2.2H_2O$.
Carbonate, $RaCO_3$.	Bromide, $RaBr_2$; $RaBr_2.2H_2O$.
	Nitrate, $Ra(NO_3)_2$.

B. Characteristics. The exceeding rarity of the compounds of radium has rendered impossible any extensive study of their chemical characteristics. Their behavior, however, is very similar to that of the barium compounds. The chloride is described as a grayish-white powder, less soluble in water and in dilute hydrochloric acid than is the chloride of barium. The bromide gives off bromine in the air, and becomes alkaline because of the formation of the hydroxide. The hydroxide absorbs carbon dioxide and becomes the carbonate, which is insoluble. Salts of radium color the flame carmine.

Certain physiological effects of radium compounds are of interest. By exposure to radium rays the skin is burned, bacteria are destroyed or hindered in development, plants lose their chlorophyll, and seeds their power of germination.

Radium is a disintegration product of uranium, and is formed directly from ionium. It is found in all uranium minerals, and in the older minerals the amount present is directly proportional to the amount of uranium in the mineral, one part of radium being associated with approximately three million parts of uranium. Radium salts have been found to emit heat at a rate corresponding to about 132 gram calories per hour per gram of radium, and are thus able to maintain their temperature considerably above that of their surroundings.

Pure radium, free from its disintegration products, gives out only α rays, but owing to the presence of these products, ordinary radium salts emit all three types of radiation. The rate of disintegration of radium corresponds to the transformation of about forty-one one-hundred thousandths of its mass per year, and the time required for exactly half of any given quantity to completely disintegrate into other elements is about 1670 years. One of the non-radioactive products of the disintegration of radium is the rare gas helium, which is formed from the expelled α particles, and the final, stable form of matter ultimately attained after the series of radioactive changes is an isotope of ordinary lead known as uranio-lead, having an atomic weight of about 206.

Radium Products. Seven successive radioactive disintegration products of radium have been identified. The first product formed is a gaseous element known as the *emanation*, which is incapable of entering into chemical combination, and in this respect is similar to argon and helium. It disintegrates rather rapidly, forming solid active products which are deposited on the walls of a vessel containing the emanation, or on the surface of any object with which it is in contact, in this manner giving rise to the phenomenon known as "induced" or "excited" activity. The emanation is condensed at the temperature of liquid air and is converted into a gas again on warming. The emanation has been found to give a characteristic bright-line spectrum, and its density has been shown to correspond to an atomic weight of about 222.

The products of radium emanation, taken in their order of production, are known as radium A, B, C, C_1, C_2, D, E and F. Radium D is commonly called "radio-lead," from the fact that it is separated with the lead from uranium minerals and is an isotope of lead. Radium F is better known as polonium. It was the first of the strongly radioactive substances to be identified, and was discovered in 1898 by P. and S. Curie. It emits only α rays and is half transformed in a period of 136 days. It has not been obtained pure in sufficient quantity to make a determination of its spectrum or atomic weight possible. It is separated with the bismuth from uranium minerals and exhibits a chemical behavior similar to that of both bismuth and tellurium. Radium A and C_1 are isotopic with polonium, Radium B with lead, Radium C and E with bismuth, and Radium C_2 with thallium.

ACTINIUM, Ac.

The radio-element known as actinium was separated from uranium minerals by Debierne in 1899. It has not yet been possible to determine either its spectrum or its atomic weight. Its rate of transformation is also unknown, but it is probably very slow, since actinium preparations retain their activity unimpaired for considerable periods. Actinium is apparently a disintegration product of uranium and occurs in exceedingly small proportions in all uranium minerals. It is separated with the rare earths and is finally obtained associated with the lanthanum.

Actinium Products. Seven successive radioactive products of the disintegration of actinium have been identified. These taken in their order are radioactinium, actinium X, actinium emanation, actinium A, B, C and D. Actinium A is isotopic with polonium, actinium B with lead, actinium C with bismuth and actinium D with thallium. Actinium emanation is a gas, apparently inert like the radium emanation. and similarly condensed at the temperature of liquid air.

THORIUM, Th, 232.4.

The radioactivity of thorium was independently discovered by C. G. Schmidt and Mme. Curie in 1898. The rate of transformation of thorium has not yet been definitely determined, but it is undoubtedly slower even than that of uranium. According to Hahn the disintegration of thorium is accompanied by the expulsion of α particles, but ordinary thorium salts containing disintegration products of thorium emit all three types of radiation.

Thorium Products. Ten successive radioactive disintegration products of thorium have been identified. These taken in the order of their production are known as mesothorium 1, mesothorium 2, radiothorium, thorium X, emanation, thorium A, thorium B, thorium C, thorium C_2 and thorium D. Mesothorium 1 and thorium X have chemical properties similar to radium and are isotopic with this element, while radio-thorium and thorium are isotopes. The thorium emanation, like the other emanations, exhibits the characteristics of an inert gas of the argon family, and is condensed at the temperature of liquid air. Of the other thorium products mesothorium 2 is an isotope of actinium, thorium A of polonium, thorium B of lead, thorium C of bismuth, thorium C_2 of polonium and thorium D of thallium.

References: Radioactive Substances and their Radiations, by E. Rutherford, Cambridge Univ. Press, 1913; The Chemistry of the Radio-Elements, by F. Soddy, Longmans, Green and Co., (second edition) 1915.

TABLE OF RADIO-ELEMENTS.

SHOWING THE TYPE OF RADIATION EMITTED BY EACH ELEMENT, ITS CONSTANT OF CHANGE, AND THE TIME REQUIRED FOR ONE-HALF OF ANY GIVEN QUANTITY TO DISINTEGRATE INTO OTHER FORMS OF MATTER.

Name.	Radiation emitted.	Disintegration Constant.	Half-value Period.
Uranium 1	α	1.3×10^{-0} (year)$^{-1}$	5.3×10^{9} years
Uranium X_1	β	2.8×10^{-2} (day)$^{-1}$	24 days
Uranium X_2	β, γ	1.0×10^{-3} (sec.)$^{-1}$	1.14 min.
Uranium 2	α	?	2×10^{6} years ?
Ionium	α	?	?
Radium	α	4.1×10^{-4} (year)$^{-1}$	1670 years
Radium emanation	α	1.8×10^{-1} (day)$^{-1}$	3.8 days
Radium A	α	3.8×10^{-3} (sec.)$^{-1}$	3 minutes
Radium B	β	4.4×10^{-4} (sec.)$^{-1}$	26 minutes
Radium C	α, β, γ	5.9×10^{-4} (sec.)$^{-1}$	19 minutes
Radium C_1	α	?	very short indeed
Radium C_2	β	1.3×10^{-3} (sec.)$^{-1}$	1.3 minutes
Radium D	β	4.2×10^{-3} (year)$^{-1}$	16 years
Radium E	β	1.4×10^{-1} (day)$^{-1}$	5 days
Radium F	α	5.1×10^{-3} (day)$^{-1}$	136 days
Actinium	no rays	?	?
Radioactinium	α	3.5×10^{-2} (day)$^{-1}$	19.5 days
Actinium X	α	6.1×10^{-2} (day)$^{-1}$	11 days
Actinium emanation	α	1.8×10^{-1} (sec.)$^{-1}$	3.9 seconds
Actinium A	α		0.002 second
Actinium B	β	3.2×10^{-4} (sec.)$^{-1}$	36 minutes
Actinium C	α	5.3×10^{-3} (sec.)$^{-1}$	2.1 minutes
Actinium D	β, γ	1.5×10^{-3} (sec.)$^{-1}$	4.6 minutes
Thorium	α	?	1.8×10^{10} years
Mesothorium 1	β	1.2×10^{-1} (year)$^{-1}$	5.5 years
Mesothorium 2	β, γ	3.1×10^{-5} (sec.)$^{-1}$	6.2 hours
Radiothorium	α	9.4×10^{-4} (day)$^{-1}$	737 days
Thorium X	α	2.2×10^{-6} (sec.)$^{-1}$	3.6 days
Thorium emanation	α	1.3×10^{-2} (sec.)$^{-1}$	54 seconds
Thorium A	α	5.0 (sec.)$^{-1}$	0.14 second
Thorium B	β	1.8×10^{-5} (sec.)$^{-1}$	10.6 hours
Thorium C	β	1.9×10^{-4} (sec.)$^{-1}$	60 minutes
Thorium C_2	α	?	exceedingly short
Thorium D	β	3.8×10^{-3} (sec.)$^{-1}$	3.1 minutes

CHAPTER IV.

THE RARE EARTHS.[*]

The rare earth elements may conveniently be classified as follows:

I. The Yttrium Group, consisting of

1. Yttrium.
2. Erbium.
3. Holmium.
4. Thulium.
5. Dysprosium.
6. Ytterbium.
7. Lutecium.
8. Celtium.

II. The Terbium Group, consisting of

1. Terbium.[†]
2. Gadolinium.[‡]
3. Europium.[‡]

III. The Cerium Group, consisting of

1. Cerium.
2. Lanthanum.
3. Neodymium.
4. Praseodymium.
5. Samarium.
6. Scandium.[§]

IV. Thorium.

V. Zirconium.

The rare earths occur so closely associated that it will be advantageous to consider their occurrence and their separation before taking them up separately.

Occurrence.[||]—Mineral sources of the rare earths are as follows:

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[*] The term *earth* is applied to certain metallic oxides which were formerly regarded as elementary bodies, as Y_2O_3, Er_2O_3, La_2O_3, and names ending in *a* are often used in designating them, as yttria, erbia, etc. The ending *um* designates the element, as yttrium, erbium, lanthanum.

[†] Placed by some in yttrium group.

[‡] Placed by some in cerium group.

[§] According to Urbain this element should hardly be classed among the rare earths (Chem. News xc, 319).

[||] See also Schilling, Das Vorkommen der seltenen Erden, R. Oldenbourg, München, 1904.

MINERAL SOURCES OF THE RARE EARTHS.

		Per cent Y Earths, Y_2O_3, etc.	Per cent Ce Earths, Ce_2O_3, etc.	Per cent ThO_2.	Per cent ZrO_2.
Adelfolite, *vid.* Zircon	....	0–trace	0–trace	0–trace	53–65
Allanite	$H\overset{II}{R}\,\overset{III}{R}_3Si_3O_{13}$	0–4	2–34	0–3	.....
Alvite, *vid.* Zircon	....	0–22	0–3	0–15	4–32
Anderbergite, *vid.* Zircon	....	7–10	0–0.2	0–1	4[illegible]–60
Arfredsonite	Complex silicate	.....	.....	.....	[illegible]–7
Astrophyllite	Complex silicate	.....	.....	.....	1–5
Auerbachite, *vid.* Zircon	....	.....	.....	.....	38–69
Auerlite,* *vid.* Thorite	....	.....	.....	.....	69–72
Azorite, *vid.* Zircon	....	.....	.....	.....	66–67
Bagrationite, *vid.* Allanite	....	.....	3–4	.....	.....
Beccarite, *vid.* Zircon	....	.....	.....	.....	62–63
Beckelith	$Ca_3(Y,Ce,La,Di)_4(Si,Zr)_3O_{15}$	2–3	59–60	.....	2–3
Bodenite, *vid.* Allanite	....	17–18	circa 18	.....	.....
Britholite, *vid.* Cappelenite	....	.....	60–61	.....	.....
Bucklandite, *vid.* Allanite	....	.....	circa 1	.....	.....
Calciothorite, *vid.* Thorite	....	.....	.....	.....	.....
Cappelenite	Complex silicate	52–53	3–[illegible]	.....	.....
Caryocerite	Complex silicate	2–3	34–36	13–14	.....
Catapleiite	$H_4(Na_2,Ca)ZrSi_3O_{11}$	.....	.....	.....	29–40
Cenosite	$H_4Ca_2(Y,Er)_2CSi_4O_{17}$	37–38	.....	.....	.....
Cererite, *vid.* Cerite	....	.....	.....	.....	.....
Cerine, *vid.* Allanite	....	.....	24–27	.....	.....
Cerinstein, *vid.* Cerite	....	.....	.....	.....	.....
*Cerite**	$(Ca,Fe)(CeO)Ce_2\cdot 3OH)(SiO_3)_7$	0–7	36–72	0–0.7	0–11
Certitanite, *vid.* Cerite	....	.....	.....	.....	.....
Clintonite,	Complex silicate	.....	.....	.....	0.7–2
Cyrtolite, *vid.* Zircon	....	8–14	0–3	0–1	41–42

* See note, page 42.

NOTE. Artini has recently described a new mineral, Bazzite, which is a complex silicate of cerium earths, the greater part being scandium (Atti R. Accad. dei Lincei. Roma [5] XXIV, I, 313).

MINERAL SOURCES OF THE RARE EARTHS—*Continued.*

		Per cent Y Earths, Y_2O_3, etc.	Per cent Ce Earths, Ce_2O_3, etc.	Per cent ThO_2.	Per cent ZrO_2.
Deweylite	$4MgO \cdot 3SiO_2 \cdot 6H_2O$	.....	3–4	.....	.....
Elpidite	$H_6Na_2ZrSi_6O_{18}$	.....	.....	.....	20–21
Emerylite	Complex silicate	.....	.....	.....	circa 4
Epidote	Complex silicate	circa 1.5	circa 1	.....	.....
Erdmannite	Complex silicate	0–2	17–35	0–10	0–5
Eucolite, *vid.* Eudialyte	....	.....	.....	.....	12–16
Eucrasite, *vid.* Thorite	....	circa 6	circa 14	circa 36	circa 0.6
Eudialyte	$Na_{13}(Ca,Fe)_6Cl(Si,Zr)_{20}O_{52}$	0–0.3	0–5	.....	11–17
Freyalite, *vid.* Thorite	....	......	31–32	28–29	circa 6
Gadolinite	$FeBe_2Y_2Si_2O_{10}$	22–46	0–51	0–0.9	.....
Gymnite, *vid.* Deweylite	....	.....	.....	.....	.....
Hainite, *vid.* Låvenite	....	.....	.....	.....	.....
Hiortdahlite	$4Ca(Si,Zr)O_3 \cdot Na_2ZrO_2F_2$	.....	.....	.....	21–22
Hyacinth, *vid.* Zircon	....	.....	.....	.....	.....
Hyposclerite	Complex silicate	.....	circa 2	.....	.....
Jargon, *vid.* Zircon	....	.....	.....	.....	.....
Johnstrupite	Complex silico-titanate	1–2	12–13	0–0.8	.....
Keilhauite*	Complex silicate	6–9	0–0.6	.....	.....
Låvenite	$R(Si,Zr)O_3 \cdot Zr(SiO_3)_2 \cdot RTa_2O_6$	.....	.....	.....	28–32
Mackintoshite	$UO_2 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 3H_2O$	1–2		circa 45	circa 1
Malacon, *vid.* Zircon	....	.....	.....	.....	.....
Manganepidote, *vid.* Epidote	....	.....	.....	.....	.....
Melanocerite	Complex silicate	9–10	circa 45	1–2	circa 0.5
Mosandrite* *vid.* Gadolinite	....	.....	.....	.....	.....
Mosandrite	Complex silico-titanate	0–3	16–26	.....	.....
Muromontite, *vid.* Allanite	....	37–38	8–10	.....	2–3
Ochroite, *vid.* Cerite	....	.....	.....	.....	.....

* See note, page 42.

MINERAL SOURCES OF THE RARE EARTHS—*Continued.*

		Per cent Y Earths, Y_2O_3, etc.	Per cent Ce Earths, Ce_2O_3, etc.	Per cent ThO_2.	Per cent ZrO_2.
Orthite,* *vid.* Allanite	....	.....	.....	.....	.....
Ostranite, *vid.* Zircon	....	.....	.....	.....	.....
Piedmontite	$HCa_2(Al,Fe,Mn)_2Si_3O_{13}$	1–2	circa 1	.....	.....
Pyrorthite, *vid.* Allanite	....	.....	.....	.....	.....
Retzian	Complex silicate	circa 10	......	.....	.....
Riebeckite, *vid.* Arfredsonite	....	.....	.....	.....	0.7–7
Rinkite	Complex silico-titanate	0–1	13–26	.....	.....
Rosenbuschite	$6CaSiO_3 \cdot 2Na_2ZrO_2F_2(TiSiO_3 \cdot TiO_3)$	.....	0.3–2.4	.....	18–20
Rowlandite	$xY_2O_3ySiO_2$	61–62	.....	.....	.....
Schelite, *vid.* Epidote	....	.....	.....	.....	.....
Serpentine	Complex silicate	.....	1–2	.....	.....
Sillimanite	Al_2SiO_5	.....	.....	.....	0–18 ?
Steenstrupine, *vid.* Caryocerite	....	0–16	14–35	2–7	.....
Tachyaphaltite, *vid.* Zircon	....	.....	.....	.....	.....
Tautolite, *vid.* Allanite	....	.....	.....	.....	.....
Thalénite	$H_2Y_4Si_4O_{15}$	58–63	.....	.....	.....
Thorite	$ThSiO_4$	0–7		48–72	0–traces
Thorogummite	$UO_3 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 6H_2O$	.....	.....	41–42	.....
Thortveitite	Complex silicate	circa 40% Sc_2O_3	.....	.....	.....
Thulite	Complex silicate	.....	circa 26	.....	.....
Tritomite	Complex silicate	0.4–3	44–59	0–9	0–4
Tscheffkinite	Complex silico-titanate	0–3	23–47	0–21	0–2
Uralorthite, *vid.* Allanite	....	.....	.....	.....	.....
Wasite, *vid.* Allanite	....	.....	.....	.....	.....
Wöhlerite	$12R(Si,Zr)O_3 \cdot RNb_2O_6$	.....	0–0.6	.....	15–23
Xanthorthite, *vid.* Allanite	....	.....	.....	.....	.....
Ytterbite, *vid.* Gadolinite	....	.....	.....	.....	.....

* See note, page 42.

MINERAL SOURCES OF THE RARE EARTHS—*Continued.*

		Per cent Y Earths, Y_2O_3, etc.	Per cent Ce Earths, Ce_2O_3, etc.	Per cent ThO_2.	Per cent ZrO_2.
Yttrialite	$\overset{III}{R}_2O_3\cdot 2SiO_2$	46–47	5–8	10–12	.....
Yttrotitanite, *vid.* Keilhauite	....	5–12	0.3–2.5	.....	.....
Zircon	$ZrSiO_4$	0–3	.....	0–2	61–70
Zirconite, *vid.* Zircon	....	.....	.....	.....	.....
Æschynite	$\overset{III}{R}_2Nb_4O_{13}\cdot\overset{III}{R}_2(Ti,Th)_5O_{13}$	1–3	15–23	13–23	0–20
Alshedite, *vid.* Titanite	....	2–3	.....	.....	.....
Annerodite	Complex	7–8	2–3	2–3	1–2
Blomstrandine-Priorite	Complex	17–20	1–4	1–8	0–1
Bragite, *vid.* Fergusonite	....	33–37	3–7	.....	0–1
Chalcolamprite, *vid.* Pyrochlore	....	.....	3–4	.....	5–6
Columbite	$(Fe,Mn)(Nb,Ta)_2O_6$	1–4	0–0.5	.....	0–0.7
Delorenzite	$2FeO\cdot UO_2\cdot Y_2O_3\cdot 24TiO_2$?	14–15	.....	.....	.....
Dysanalyte	Complex titano-niobate	0–5	0.1–6	.....	.....
Endeiolite, *vid.* Pyrochlore	....	.....	4–5	.....	3–4
Eucolite-titanite, *vid.* Titanite	....	circa 0.6	2–3	circa 0.2	.....
Euxenite	$\overset{III}{R}(NbO_3)_3\cdot\overset{III}{R}_2(TiO_3)_3\tfrac{3}{2}H_2O$	13–30	2–8	0–6	0–2
Fergusonite	$\overset{III}{R}(Nb,Ta)O_4$	30–46	0–9	0–3	0–7
Fluochlore, *vid.* Pyrochlore	....	0.7–0.9	5–15	.....	0–5
Guarinite	$CaTiSiO_5$	circa 1	3–4	.....	.....
Hatchettolite	$R(Nb,Ta)_2O_6\cdot H_2O$	0–2		.....	.....
Hielmite	Complex	1–5	0.4–1	.....	.....
Knopite, *vid.* Perovskite	....	.....	4–7	.....	0–1
Kochelite, *vid.* Fergusonite	....	17–18	.....	1–2	12–13
Koppite, *vid.* Pyrochlore	....	.....	4–11		0–5

MINERAL SOURCES OF THE RARE EARTHS—*Continued.*

		Per cent Y Earths, Y_2O_3, etc.	Per cent Ce Earths, Ce_2O_3, etc	Per cent ThO_2.	Per cent ZrO_2.
Leukosphenite	Complex silico-titanate	.....	.....	.....	3–4
Loranskite, *vid.* Euxenite	....	10	3	20	.....
Madupite	Silico-titano-carbonate	.....	0.1	.....	.....
Marignacite, *vid.* Pyrochlore	....	circa 5	13–14	0.2	.....
Microlite	$Ca_2Ta_2O_7$	0–7	0–4	.....	.....
Nephelinsyenite	Complex silico-titanate	.....	.....	.....	circa 1
Niobite, *vid.* Columbite	....	.....	.....	.....	0.1–0.5
Nohlite, *vid.* Samarskite	....	14–15	0.25	.....	2–3
Oerstedite, *vid.* Zircon	....	.....	.....	.....	.....
Orendite	Complex silico-titano-carbonate	.....	.....	.....	0.22
Perovskite	$CaTiO_3$	5–6	0.1	.....	.....
Polycrase	$\overset{III}{R}(NbO_3)_3\cdot 2\overset{III}{R}(TiO_3)_3\cdot 3H_2O$	20–32	0–3	0–3.5	.....
Polymignite	$5RTiO_3\cdot 5RZrO_3\cdot R(Nb,Ta)_2O_6$	2–3	2–11	3–4	29–30
Pyrochlore*	$RNb_2O_6\cdot R(Ti,Th)O_3$	.....	5–10	0–8	.....
Rogersite	Complex	60–61	.....	.....	.....
Samarskite	$\overset{II}{R}_3\overset{III}{R}_2(Nb,Ta)_6O_{21}$	5–21	2–5	0–6	0–4
Sipylite	Complex	27–28	9–10	.....	circa 2
Tantalite	$FeTa_2O_6$	.....	.....	.....	1–11
Tapiolite, *vid.* Tantalite	....	.....	.....	.....	.....
Titanite	$CaTiSiO_5$	0.5–2		.....	.....
Tyrite, *vid.* Fergusonite	....	28–36	4–9	.....	0–3
Vietinghofite, *vid.* Samarskite	....	6–7	1–2	.....	circa 1
Wiikite†	....	7–8	2–3	5–6	+TiO_2 23–24
Ytteroilmenite, *vid.* Samarskite	....	.....	.....	.....	.....
Yttrocrasite	Complex titanate	25–26	2–3	8–9	.....

* See note, page 42.

† Contains more than 1% of Sc_2O_3. See note, page 42.

MINERAL SOURCES OF THE RARE EARTHS—*Continued.*

		Per cent Y Earths, Y_2O_3, etc.	Per cent Ce Earths, Ce_2O_3, etc.	Per cent ThO_2.	Per cent ZrO_2.
Yttrotantalite	$\overset{II}{R}\overset{III}{R}_2(Ta,Nb)_4O_{15}\cdot 4H_2O$	17–38	0–2	.....	.....
Yttrotitanite, *vid.* Keilhauite	....	.....	.....	.....	.....
Zirkelite	$(Ca,Fe)O\cdot 2(Zr,Ti,Th)O_2$	0–2	2–3	0–7	50–53
Apatite	$Ca_4P_3O_{12}(Ca(F)(Cl))$	.....	0–5	.....	.....
Castelnaudite, *vid.* Xenotime	....	.....	.....	.....	.....
Churchite	$\overset{II}{R}_3(PO_4)_2\cdot 4H_2O$	.....	50–51	.....	.....
Cryptolite, *vid.* Monazite	....	.....	.....	.....	.....
Edwarsite, *vid.* Monazite	....	.....	.....	.....	.....
Eremite, *vid.* Monazite	....	.....	.....	.....	.....
Florencite	Complex phospho-silicate	.....	28	.....	.....
Hussakite, *vid.* Xenotime	....	.....	.....	.....	.....
Mengite, *vid.* Monazite	....	.....	.....	.....	.....
Monazite	$(Ce,La,Di)PO_4$	0–5	39–74	0–18	0–7
Monazitoid *vid.* Monazite	....	.....	.....	.....	.....
Rhabdophanite	$RPO_4\cdot H_2O$	2–10	53–58	.....	.....
Scovillite, *vid.* Rhabdophanite	....	.....	.....	.....	.....
Turnerite, *vid.* Monazite	....	.....	.....	.....	.....
Xenotime	YPO_4	54–64	0–11	0–3	0–2
Ancylite	$4Ce(OH)CO_3\cdot 3SrCO_3\cdot 3H_2O$	.....	46–47	0.2	.....
Bastnäsite	$(Ce,La,Di)_2(CO_3)_3(Ce,La,Di)F_3$	.....	64–93	0–10	.....
Cordylite, *vid.* Parisite	....	.....	49–50	0.3	.....
Hamartite, *vid.* Bastnäsite	....	.....	.....	.....	.....
Hydrocerite, *vid.* Lanthanite	....	.....	.....	.....	.....
Lanthanite	$La_2(CO_3)_3\cdot 9H_2O$	.....	55La_2O_3	.....	.....

MINERAL SOURCES OF THE RARE EARTHS—*Continued.*

		Per cent Y Earths, Y_2O_3, etc.	Per cent Ce Earths, Ce_2O_3, etc.	Per cent ThO_2.	Per cent ZrO_2.
Musite, *vid.* Parisite	....	.....	.....	.....	.....
Parisite	$(CaF)(CeF)Ce(CO_3)_3$	0–2.5	51–64	.....	.....
Synchisite	$CeFCa(CO_3)_2$	1–2	50–51	0–0.3	.....
Tengerite	$Y_2(CO_3)_3$	40–41	circa 7	.....	.....
Weibyeite, *vid.* Parisite	....	.....	66–67	.....	.....
Fluocerite	$R_2O_3 \cdot 4RF_3$	1–4	81–83	.....	.....
Hydrofluocerite, *vid.* Fluocerite	....	.....	.....	.....	.....
Tysonite	$(Ce,La,Di)F_3$	.....	69–70	.....	.....
Yttrocerite	$2(2\overset{III}{R}F_3 \cdot 9CaF_2) \cdot 3H_2O$	8–15	9–16	.....	.....
Danburite	$CaB_2Si_2O_8$	0.85	.....	.....	.....
Homilite	$(Ca,Fe)_3B_2Si_2O_{10}$	.....	0.2–2.5	.....	.....
Nordenskiöldine	$CaSn(BO_3)_2$	.....	.....	.....	0.9
Baddeleyite	ZrO_2	.....	.....	.....	96–97
Brazilite, *vid.* Baddeleyite	....	.....	.....	.....	.....
*Thorianite,** *vid.* Uraninite	....	.....	1–8	70–80	0–3.5
Pyrolusite	MnO_2	0.1	.....	.....	.....
Nivenite, *vid.* Uraninite	....	11–12	.....	7–8	.....
Uraninite	Complex uranate	0–10	0–3	1–11	0–8
Uranothorite, *vid.* Thorite	....	.....	.....	.....	.....
Uranophane, *vid.* Uraninite	....	.....	.....	.....	.....
Uranotil, *vid.* Uraninite	....	.....	.....	.....	.....
Yttrogummite, *vid.* Uraninite	....	.....	.....	.....	.....

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* Crookes (Proc. Royal Soc. (London) LXXX (A), 516), has shown scandium to be widely distributed. The minerals starred contain over 0.01%. Eberhard, in examination of over 350 minerals and rocks, found the spectrum of scandium (group of lines between 3535.86 and 3651.98, with brightest at 3613.98) rarely absent. He mentions wolframite, cassiterite and monazite especially. (Sitzungber. Akad. Sci. Berlin, 1908, 851; and 1910, 404.)

NOTE. By the study of cathodic phosphorescence applied to many specimens of scheelites, de Rohden observed the spectra of Dy, Er, Eu, Nd, Pr, Sm, and Tb (Compt. rend. CLIX, 318).

Separation. The methods of separation here enumerated without reference to original sources are described in full in Böhm's "Darstellung der seltenen Erden," volume 1, pages 108 to 490.

(1) Ignition of the nitrates, carbonates, or oxalates, and treatment of the product with ammonium nitrate, ammonium chloride, or dilute acid.
(2) Treatment of suspended hydroxides with chlorine.
(3) Oxidation with potassium permanganate.
(4) Treatment with peroxides, as PbO_2, etc.
(5) Oxidation with hydrogen dioxide or sodium dioxide.
(6) Treatment with persulphates.
(7) Treatment with the electric current. (*Vid.* also (33).)
(8) Formation of basic nitrates.
    (*a*) By treating the nitrates with oxides.
    (*b*) By treating the neutral nitrates with hot water.
(9) Formation of basic chlorides.
    (*a*) By treating the chlorides with water.
    (*b*) By treating the chlorides with magnesium oxide or copper oxide.
(10) Formation of basic sulphates by the action of water.
(11) Fractional precipitation with ammonium hydroxide.
(12) Fractional precipitation with sodium or potassium hydroxide.
(13) Partial precipitation with anilin.
(14) Precipitation by alkali hyponitrides.
(15) Precipitation by sulphurous acid and sulphites.
(16) Precipitation by sodium thiosulphate.
(17) Precipitation by carbonates.
(18) Precipitation as chromates.*
(19) Precipitation by formates.
(20) Precipitation by acetates.
(21) Action of dilute acid upon the oxalates.
(22) Precipitation as the sulphates.

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* *Vid.* James, Jour. Amer. Chem. Soc. xxxvi, 638, 1418; also Egan and Balke, ibid. xxxv, 376.

(23) Fractional crystallization of the nitrates.

(24) Action of alcohol upon the nitrates.

(25) Action of (*a*) acetylacetone, (*b*) ethylsulphate, (*c*) salts of sulphanilic acid.

(26) Fractional crystallization of the double salts:
- (*a*) Double sulphates with alkali sulphates.
- (*b*) Double nitrates with ammonium nitrate.
- (*c*) Double nitrates with magnesium nitrate.
- (*d*) Double nitrates with bismuth nitrate.
- (*e*) Double fluorides with alkali and magnesium fluorides.

(27) Action of (*a*) neutral or acid potassium oxalate; (*b*) ammonium oxalate.

(28) Fractional crystallization of the bromates (James, Jour. Amer. Chem. Soc. xxx, 182).

(29) Fractional precipitation of the succinates (Lenher, Jour. Amer. Chem. Soc. xxx, 572).

(30) Action of ammonium carbonate upon the oxalates (James, Jour. Amer. Chem. Soc. xxix, 495).

(31) Fractional precipitation by potassium stearate (Stoddart and Hill, Jour. Amer. Chem. Soc. xxxiii, 1076).

(32) Fractional crystallization of the picrates (Dennis and Bennett, Jour. Amer. Chem. Soc. xxxiv, 7; Dennis and Rhodes, ibid. xxxvii, 807).

(33) Fractional electrolysis of the nitrates and the chlorides (Dennis, Lemon, van der Meulen and Ray, Jour. Amer. Chem. Soc. xxxvii, 131, 1963; xl, 174.)

(34) Fractional precipitation of the nitrites (James and Holden, Jour. Amer. Chem. Soc. xxxvi, 1418).

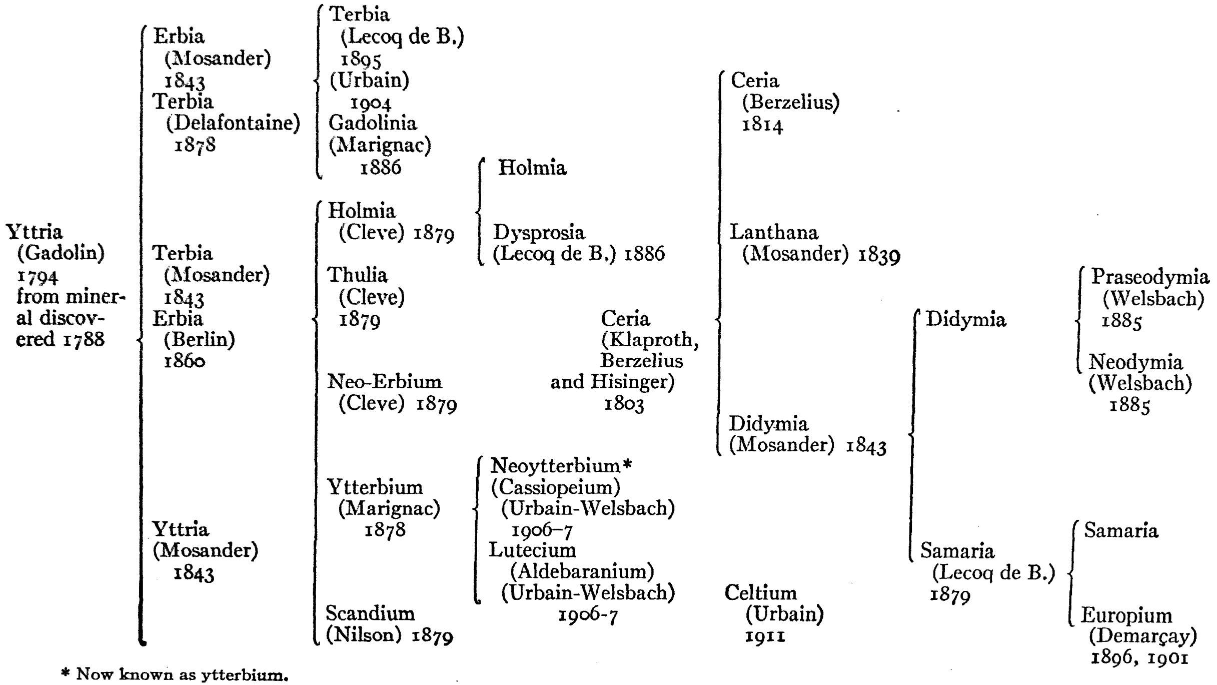
(35) Fractional solution of the hydroxides by bromine (Browning, Compt. rend. clviii, 1679).

(36) Fractional precipitation of the cobalticyanides (James and Bonardi, Jour. Amer. Chem. Soc. xxxvii, 2645).

(37) Fractional crystallization of the dimethyl phosphates (Jordan and Hopkins, Jour. Amer. Chem. Soc. xxxix, 2614).

DIAGRAM SHOWING THE ORDER OF DISCOVERY OF THE RARE EARTHS.

(Adapted with modifications and additions from Abegg's Handbuch der Anorganischen Chemie and Roscoe's Treatise on Chemistry.)


Yttria (Gadolin) 1794 from mineral discovered 1788
Erbia (Mosander) 1843 Terbia (Delafontaine) 1878
Terbia (Lecoq de B.) 1895 (Urbain) 1904 Gadolinia (Marignac) 1886
Terbia (Mosander) 1843 Erbia (Berlin) 1860
Holmia (Cleve) 1879
Holmia
Dysprosia (Lecoq de B.) 1886
Thulia (Cleve) 1879
Neo-Erbium (Cleve) 1879
Ytterbium (Marignac) 1878
Neoytterbium* (Cassiopeium) (Urbain-Welsbach) 1906–7
Lutecium (Aldebaranium) (Urbain-Welsbach) 1906-7
Scandium (Nilson) 1879
Yttria (Mosander) 1843
Ceria (Klaproth, Berzelius and Hisinger) 1803
Ceria (Berzelius) 1814
Lanthana (Mosander) 1839
Didymia (Mosander) 1843
Celtium (Urbain) 1911
Didymia
Praseodymia (Welsbach) 1885
Neodymia (Welsbach) 1885
Samaria (Lecoq de B.) 1879
Samaria
Europium (Demarçay) 1896, 1901

* Now known as ytterbium.

(38) Fractional precipitation of the glycolates (Jordan and Hopkins, *ibid.*).

The separation of the rare earths cannot be made with quantitive accuracy. For working schemes, however, the student is referred to methods worked out by James (Jour. Amer. Chem. Soc. XXX, 979; and XXXIV, 757) and diagrammatically shown on pp. 216–18. These are the only schemes of separation that have come to the notice of the author, and they are followed in this book where methods are described at all in detail. It may be added that Urbain (Jour. chim. phys. IV, 31) has arranged the rare earths according to their solubilities as follows: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium.

Urbain has used the magnetic balance successfully as a means of identification and also as a test for purity in connection with processes of fractionation. The oxides are used in this process, and the coefficient of magnetization being $X \times 10^{-6}$, the following values have been determined: Sc, −0.05; Y, −0.14; La, −0.18; Nd, 33.5; Sm, 6.5; Eu, 33.5; Gd, 161; Tr, 237; Dy, 290 (Compt. rend. CXLVII, 1286; CL, 913; CLII, 141).

I. THE YTTRIUM GROUP.

1. **YTTRIUM,** Y, 88.7.

Discovery. In the year 1794, Gadolin (Kongl. Vet. Acad. Handl. XV, 137; Crell Annal. (1796) 1,313) discovered a new earth in a mineral later called Gadolinite, which had been discovered by Arrhenius and described by Geyer in 1788 (Crell Annal. (1788) 1,229). In 1797 Eckeberg confirmed Gadolin's discovery and named the new earth Yttria (Kongl. Vet. Acad. Handl. XVIII, 156; Crell Annal. (1799) II, 63), deriving the name from Ytterby, the source of the mineral.

Occurrence. Yttrium occurs always in combination. Its chief sources are the minerals gadolinite and xenotime, and monazite residues (*vid.* Occurrence of Rare Earths, page 35).

Extraction. The following are common methods for the extraction of yttrium salts from minerals:

(1) *From gadolinite (or any other silicate).* The finely powdered mineral is mixed with common sulphuric acid until the mass has the consistency of thick paste. It is then heated until dry and hard, pulverized, and extracted with cold water. From this extraction the oxalates are precipitated by the addition of oxalic acid; they are then washed, dried, and heated at 400° C. The oxides thus obtained are dissolved in sulphuric acid, and the solution is saturated with potassium or sodium sulphate. The double sulphates of the cerium group are precipitated, and the members of the yttrium group remain in solution.

(2) *From gadolinite.* The mineral is decomposed by aqua regia (*vid.* Experiment 1).

(3) *From samarskite.* The mineral is decomposed by hydrofluoric acid. The niobic and tantalic acids go into solution, and the yttrium earths, together with uranium oxide, remain (Lawrence Smith, Amer. Chem. Jour. v, 44).

The Element. *A. Preparation.* Elementary yttrium may be obtained (1) by heating the chloride with potassium (Berzelius); (2) by subjecting the melted double chloride of sodium and yttrium to electrolysis (Cleve, Bull. Soc. Chim. d. Paris [2] XVIII, 193); (3) by heating the oxide with magnesium (Winkler, Ber. Dtsch. chem. Ges. XXIII, 787).

B. Properties. Yttrium is a grayish-black powder, which decomposes water only slightly at ordinary temperatures, but more rapidly on boiling, forming the oxide. Ignited on platinum in the air, it burns to the oxide with a brilliant light; in oxygen with a very intense glow. It is very soluble in dilute acids, including acetic, but is only slightly soluble in concentrated sulphuric acid. It decomposes potassium hydroxide at the boiling temperature. Its melting-point is 1490° C.

Compounds. *A. Typical forms.* The following are typical compounds of yttrium:

Oxide, Y_2O_3.
Hydroxide, $Y(OH)_3$.
Carbonates, $Y_2(CO_3)_3+3H_2O$; $Y_2(CO_3)_3\cdot Na_2CO_3+4H_2O$; $Y_2(CO_3)_3\cdot(NH_4)_2CO_3+2H_2O$.
Chlorides, YCl_3; YCl_3+6H_2O; $YCl_3\cdot 3HgCl_2+9H_2O$; $YCl_3\cdot 2AuCl_3+16H_2O$; $2YCl_3\cdot 3PtCl_2+24H_2O$.
Chlorate, $Y(ClO_3)_3+8H_2O$.
Perchlorate, $Y(ClO_4)_3+8H_2O$.
Bromides, YBr_3; YBr_3+9H_2O.
Bromate, $Y(BrO_3)_3+9H_2O$.
Iodide, YI_3.
Iodate, $Y(IO_3)_3+3H_2O$.
Periodate, $Y_2O_3\cdot I_2O_7+8H_2O$.
Fluoride, $YF_3+0.5H_2O$.
Nitrates, $Y(NO_3)_3+6H_2O$; $2Y_2O_3\cdot 3N_2O_5+9H_2O$.
Cyanides, $YKFe(CN)_6+2H_2O$; $Y(SCN)_3+6H_2O$.
Sulphates, $Y_2(SO_4)_3+8H_2O$; $Y_2(SO_4)_3\cdot 4K_2SO_4$; $Y_2(SO_4)_3\cdot Na_2SO_4+2H_2O$.
Sulphite, $Y_2(SO_3)_3+3H_2O$.
Seleniates, $Y_2(SeO_4)_3+8H_2O$; $Y_2(SeO_4)_3\cdot K_2SeO_4+6H_2O$; $Y_2(SeO_4)_3\cdot(NH_4)_2SeO_4+6H_2O$.
Selenites, $Y_2(SeO_3)_3+12H_2O$; $Y_2O_3\cdot 4SeO_2+4H_2O$.
Sulphide, Y_2S_3.
Oxalate, $Y_2(C_2O_4)_3+9H_2O$.
Phosphates, YPO_4; $Y(PO_3)_3$; $YHP_2O_7+3.5H_2O$.
Chromate, $Y_2(CrO_4)_3\cdot K_2CrO_4+xH_2O$.
Tungstate, $Y_2(WO_4)_3+6H_2O$.
Carbide, YC_2.
Organic compounds, *vid.* Platt and James, Jour. Amer. Chem. Soc. XXXIII, 1330.

B. Characteristics. The compounds of yttrium have few characteristic reactions. They resemble quite closely the compounds of aluminum, but yttrium differs from aluminum in having a hydroxide insoluble in excess of sodium or potassium hydroxide and in forming no alums. The salts of yttrium give no absorption spectra. Yttrium sulphate differs from the sulphate of cerium in forming no insoluble double sulphate with potassium or sodium sulphate. Most of the rare earth compounds except the sulphate, nitrate and halogen salts are insoluble.

Estimation. Yttrium is generally weighed as the oxide, (Y_2O_3), which has been obtained by the ignition of the hydroxide or the oxalate (*vid.* James, Jour. Amer. Chem. Soc. XXXVI, 909).

Separation. In the course of analysis the yttrium earths are precipitated with the aluminum group. They may be separated from aluminum by precipitation with oxalic acid or ammonium oxalate in faintly acid solution; in this reaction they resemble the other members of the rare-earth group (Ce, La, Pr, Nd, Th, Zr, etc.). They may be separated from these by saturating a solution of the sulphates with potassium sulphate; the yttrium earths do not form a double sulphate insoluble in potassium sulphate as do the others.

For the separation of yttrium from the very rare members of its group Methods 8, 9(*a*), 11, 18, 21, 28, 34 and 36 (page 43) have been used. James recommends the fractional crystallization of the bromates (28), and finds the yttrium in the fraction between the holmium and the erbium. Taking the fractions free from holmium, he converts them into the neutral nitrates. These nitrates of yttrium and erbium are boiled with the addition of magnesium oxide until the liquid shows no absorption bands of erbium.

EXPERIMENTAL WORK ON YTTRIUM.

Experiment 1. *Extraction of yttrium salts from gadolinite* ($Be_2FeY_2Si_2O_{10}$). Warm 5 grm. of finely powdered mineral with aqua regia until it is completely decomposed. Evaporate on a water-bath and desiccate to remove the silica. Extract with hot water and a little hydrochloric acid, and add to the extract ammonium oxalate until precipitation ceases. Filter off the precipitate, which consists of the oxalates of the yttrium and cerium groups, together with traces of the oxalates of manganese and calcium; dry and ignite. Dissolve in a small amount of hydrochloric acid the oxides thus obtained, and saturate the solution with potassium sulphate*; this precipitates the members of the cerium group as the double sulphates. Filter, and wash with a solution of potassium sulphate. From the filtrate precipitate the yttrium earths by an alkali hydroxide or oxalate. To remove the manganese and calcium, dissolve the precipitate in nitric acid, evaporate to dryness, and heat until the manganese salt is decomposed. Extract with water, filter off the oxide of manganese, treat the filtrate with ammonium hydroxide, and stir thoroughly. The calcium hydroxide will be dissolved, and the yttrium earths precipitated.

Experiment 2. *Precipitation of yttrium hydroxide* ($Y(OH)_3$). (*a*) To a solution of an yttrium salt add ammonium hydroxide.

(*b*) Repeat the experiment, using sodium or potassium hydroxide.

Note the insolubility in excess in each case.

(*c*) Precipitate yttrium hydroxide by the action of ammonium sulphide.

Experiment 3. *Precipitation of yttrium carbonate* ($Y_2(CO_3)_3$). (*a*) To a solution of an yttrium salt add ammonium carbonate.

(*b*) Repeat the experiment, using sodium or potassium carbonate.

Note the solubility in the cold upon the addition of an excess of the alkali carbonates, and the reprecipitation on boiling.

(*c*) Try the action of the common acids upon yttrium carbonate.

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* Or, with sodium sulphate (James, Jour. Amer. Chem. Soc. xxxv, 559).

Experiment 4. *Precipitation of yttrium oxalate* ($Y_2(C_2O_4)_3$). To a solution of an yttrium salt add a solution of either oxalic acid or an alkali oxalate.

Experiment 5. *Precipitation of yttrium phosphates* ($Y_2(HPO_4)_3$; YPO_4). To a solution of an yttrium salt add sodium phosphate in solution (Na_2HPO_4). The precipitate is said to be of the acid form $Y_2(HPO_4)_3$. The neutral phosphate (YPO_4) is formed by treating an yttrium salt in solution with an ammoniacal phosphate.

Experiment 6. *Precipitation of yttrium ferrocyanide* ($YKFe(CN)_6$). To a solution of an yttrium salt add potassium ferrocyanide.

Experiment 7. *Precipitation of yttrium chromate* ($xY_2(CrO_4)_3 \cdot yY_2O_3$). To a solution of an yttrium salt add a solution of potassium chromate, and neutralize if necessary.

Experiment 8. *Precipitation of yttrium fluoride* (YF_3). To a solution of an yttrium salt add potassium fluoride.

Experiment 9. *Negative tests of yttrium salts.* Note that hydrogen sulphide gives no precipitate with yttrium salts, and that saturation of a solution of an yttrium salt with potassium or sodium sulphate gives no insoluble double salt.

2. **ERBIUM,** Er, 167.7
3. **HOLMIUM,** Ho, 163.5
4. **THULIUM,*** Tm, 168.5
5. **DYSPROSIUM,** Dy, 162.5
6. **YTTERBIUM,** Yb, 173.5
7. **LUTECIUM,** Lu, 175
8. **CELTIUM,** Ct.

Discovery. In 1843 Mosander (J. pr. Chem. xxx, 288) announced, as the result of his investigation of yttria, its separation into three earths, two white and one yellow. To the less basic of the white oxides he gave the name Terbium earth, to the more basic the original name Yttrium earth, and the yellow oxide he called Erbium earth.

In 1879 Cleve (Compt. rend. LXXXIX, 478), while working on erbium earth, discovered two elements, Holmium and Thulium, which he separated as the oxides.

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* For the most recent work upon this earth, *vid.* James, Jour. Amer. Chem. Soc. XXXIII, 1332, 1363.

Seven years later Lecoq de Boisbaudran (Compt. rend. CII, 1004), announced the isolation of a new earth from the oxide of holmium, namely, that of Dysprosium.

In 1878 Marignac (Compt. rend. LXXXVII, 578) found in gadolinite the oxide of a new element which he named Ytterbium.

In 1906 Auer von Welsbach (Monatshefte f. Chem. XXVII, 935) announced that he had decomposed ytterbium by the action of ammonium oxalate on the double ammonium oxalate, and in 1907 Urbain (Compt. rend. CXLV, 759; Chem. News XCVI, 271) stated that by subjecting Marignac's ytterbium to fractional crystallization in nitric acid he had separated it into two elements, which he called Neoytterbium* and Lutecium.

Four years later, while subjecting the gadolinite earths to fractional crystallization in nitric acid, Urbain obtained a mother liquor from which he separated an oxide of very low magnetic susceptibility. The arc spectrum showed many new lines, some very intense. The new earth proved to be in chemical character between lutecium and scandium. The name Celtium was proposed, and the symbol Ct (Compt. rend. CLII, 141; Chem. Ztg. XXXV, 161).

In 1899 Crookes (Chem. News LXXIX, 212) separated from the yttrium earths by fractional fusion of the nitrates and fractional crystallization of the oxalates a new substance having a group of lines in the ultra violet. This substance he at first called Monium and later Victorium (Proc. Royal Soc. LXV, 237). Urbain, however, considers it to be identical with gadolinium (Jour. chim. phy. IV, 321).

Occurrence. These very rare earths are found in small quantities and varying proportions associated with yttria (*vid.* Occurrence of Rare Earths, page 35). Their chief sources are as follows: of erbium, gadolinite, yttrotantalite, euxenite, sipylite, xenotime; of ytterbium, gadolinite, sipylite, xenotime, euxenite; of holmium, thulium and dysprosium, gadolinite, keilhauite, euxenite, samarskite.

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* Now known as ytterbium.

Extraction. Methods for the extraction of the yttrium earths have been already given (*vid.* Extraction of Yttrium, page 46).

	Er	Yb
Oxides	Er_2O_3 Er_2O_5	Yb_2O_3
Hydroxides	$Er_2O(OH)_4$	$Yb_2O_3+6H_2O$
Chlorides	$ErCl_3$	$YbCl_3+3H_2O$
Bromides	$ErBr_3+9H_2O$	
Iodide	ErI_3	
Fluoride	ErF_3	
Chlorate	$Er(ClO_3)_3+8H_2O$	
Perchlorate	$Er(ClO_4)_3+8H_2O$	
Bromate	$Er(BrO_3)_3+9H_2O$	
Iodate	$Er(IO_3)_3+3H_2O$	
Sulphite	$Er_2(SO_3)_3+3H_2O$	
Sulphates	$Er_2(SO_4)_3+8H_2O$	$Yb_2(SO_4)_3+8H_2O$
Double sulphates	$Er_2(SO_4)_3 \cdot 3K_2SO_4$ $Er_2(SO_4)_3 \cdot 5Na_2SO_4$ $Er_2(SO_4)_3 \cdot (NH_4)_2SO_4$	
Dithionate	$Er_2(S_2O_6)_3+18H_2O$	
Selenites	$Er_2(SeO_3)_3+5H_2O$	$Yb_2(SeO_3)_3$
Seleniate	$Er_2(SeO_4)_3+5H_2O$	
Nitrate	$Er(NO_3)_3+6H_2O$	
Phosphate	$ErPO_4+H_2O$	
Pyrophosphate	$Er_2H_2(P_2O_7)_2+7H_2O$	
Carbonate	$Er_2O_3 \cdot 2CO_2+2H_2O$	
Oxalates	$Er_2(C_2O_4)_3+12H_2O$	$Yb_2(C_2O_4)_3+10H_2O$
Acetates	$Er(C_2H_3O_2)_3+2H_2O$	$Yb(C_2H_3O_2)_3+2H_2O$
Sulphide	Er_2S_3	

Compounds. *A. Typical forms.* In the table on this page are given typical compounds of erbium and ytterbium.

B. Characteristics. In general chemical behavior the compounds of the yttrium earths resemble closely those of yttrium. The salts of erbium are of a rosy tint and give absorption bands. The oxide is yellowish. Ytterbium forms colorless compounds and gives no absorption bands. The compounds of holmium, thulium, dysprosium, lutecium, and celtium have not been sufficiently investigated to warrant description. The identification of members of this group is made by the methods of spectrum analysis.

Separation. For the separation of erbium from the other members of the yttrium group Methods 8, 9, 11, 12, 13, 20, 26(*a*), and 28 (page 43) are used. James obtains erbium by his bromate process (*vid.* Separation of Yttrium, page 49) in the fraction between yttrium and thulium.

In separating ytterbium, Methods 8, 9, 11, 21, 26(*a*), and 28 are recommended. In the bromate process this earth is to be found in the mother liquor after the separation of the fractions containing the other members of the group.

Holmium has been separated by Methods 1, 11, 13, 26(*a*), and 28. It is found in the bromate process in the fraction between dysprosium and yttrium.

For thulium Methods 8, 25(*b*), and 28 have been recommended. It crystallizes in the bromate process in the last fraction following the erbium.

Dysprosium has been separated by Methods 11, 26(*a*), and 28. The bromate of this earth crystallizes between terbium and holmium.

II. THE TERBIUM GROUP.

1. **TERBIUM,*** Tr, 159.2 2. **GADOLINIUM,** Gd, 157.3
3. **EUROPIUM,** Eu, 152.

Discovery. Terbium was first isolated by Mosander in 1843 (*vid.* Discovery of Erbium).

In 1886 Marignac and Lecoq de Boisbaudran (Compt. rend. CII, 902) separated from terbium earth the oxide of an unknown element named by them Gadolinium.

Demarçay, in 1901 (Compt. rend. CXXXII, 1484), isolated a colorless earth closely associated with samarium, and named the new element Europium. This earth, the existence of which had for some years been recognized by himself and by others, had been designated by him as Σ, and by Lecoq de Boisbaudran as Zε.

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* For review of recent work *vid.* James, J. Amer. Chem. Soc. XXXIII, 816; XXXVI, 2060; XXXVII, 2652; XXXVIII, 873.

Occurrence. These earths are found in small quantities associated with the yttrium earths (*vid.* Occurrence of Rare Earths, page 35). The chief sources of terbium are gadolinite, samarskite, euxenite, and monazite; of gadolinium, samarskite and orthite; of europium, samarskite, orthite, cerite, gadolinite, keilhauite.

Extraction. These earths are extracted from minerals with the members of the yttrium group (*vid.* Extraction of Yttrium, page 46).

Compounds. *A. Typical forms.* The following are typical compounds of terbium and gadolinium:

	Tr	**Gd**
Oxide	Tr_2O_3	
Hydroxide	$Tr_2O_3 + 6H_2O$	
Chloride		$GdCl_3 + 6H_2O$
Bromide		$GdBr_3 + 6H_2O$
Sulphate	$Tr_2(SO_4)_3 + 8H_2O$	
Double sulphate		$Gd_2(SO_4)_3 \cdot K_2SO_4 + 2H_2O$
Nitrates	$Tr(NO_3)_3 + 6H_2O$	$Gd(NO_3)_3 + 5H_2O$
Double nitrate		$2Gd(NO_3)_3 \cdot 3Ni(NO_3)_2 + 24H_2O$
Carbonates	$Tr_2(CO_3)_3 + xH_2O$	$Gd_2(CO_3)_3 + 13H_2O$
Acetates	$Tr(C_2H_3O_2)_3$	$Gd(C_2H_3O_2)_3 + 4H_2O$

B. Characteristics. The compounds of the terbium earths are very similar in chemical form and behavior to those of the yttrium earths. The members of this group are distinguished from the yttrium earths on the one hand, and from the cerium earths on the other, in that their double potassium sulphates are more insoluble in a saturated solution of potassium sulphate than the corresponding salts of the former group, and less insoluble than those of the latter.

Separation. Methods 8, 11, 18, 19, 26 (*a*), and 28 (page 43) have been used in separating terbium from other rare earths. James separates terbium from the cerium earths by saturation with sodium sulphate. On conversion of the yttrium earths together with terbium into the bromates, and crystallization, the terbium separates in the first fraction. Gadolinium has been separated by Methods 11, 23, 26 (*a*), (*b*), (*c*), (*d*), 29, 37 and 38. James classifies it in the cerium group, and by crystallization of the double magnesium nitrates separates it in the last fraction.

Methods 26 (*c*) and (*d*) have been especially effective in separating europium. James finds the main portion of the europium with the cerium earths, especially samarium, after the treatment with sodium sulphate. When lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium are subjected to fractional crystallization as the double magnesium nitrates, europium appears in the last fraction before gadolinium and following samarium.

III. THE CERIUM GROUP.

1. CERIUM, Ce, 140.25.

Discovery. In the course of the analysis of a mineral from Riddarhyttan, Sweden, in 1803, Klaproth discovered an earth which, while resembling yttria in many of its reactions, differed from it in being insoluble in carbonate of ammonium, and in acquiring, when ignited, a light brown color. Because of this latter peculiarity, the name Ochroite suggested itself to him, from ’ωχρός, *yellow brown* (Phil. Mag. XIX, 95). At the same time, and independently of Klaproth, Berzelius and Hisinger made the same discovery. Their name for the new element was Cerium, chosen in honor of the discovery of the planet Ceres by Piazzi in 1801 (Phil. Mag. XX, 155; XXII, 193).

Occurrence. Cerium is found in many minerals, associated, usually, with other members of the rare earth group (*vid.* Occurrence of Rare Earths, page 35). Its chief sources are allanite, monazite, and cerite.

Extraction. Cerium is generally extracted from cerite through decomposition of the mineral by heating it with strong sulphuric acid (*vid.* Experiment 1). The decomposition may be accomplished also by the action of a mixture of strong hydrochloric and nitric acids, but better results may be expected by the former method.

The Element. *A. Preparation.* Elementary cerium may be obtained (1) by reducing the chloride with sodium or potassium (Mosander); (2) by subjecting the double chloride of cerium and sodium to electrolysis (Pogg. Annal. CLV, 633).

B. Properties. In appearance cerium resembles iron. While fairly stable in dry air, it oxidizes quickly in moist air. It takes fire more easily than magnesium, and melts at a lower temperature than silver and at a higher temperature than antimony. It is soluble in dilute acids, but is not attacked by concentrated sulphuric or nitric acid. It combines with chlorine, bromine, and iodine, forming salts. Its specific gravity is .7, and its melting-point 640° C. It forms alloys with iron, aluminum, zinc, and magnesium, and combines with boron and silicon. Many of these alloys are pyrophoric (*vid.* Levy, Rare Earths, p. 314).

Compounds. *A. Typical forms.* The following are typical forms of the two classes of cerium compounds:

Oxides	Ce_2O_3	CeO_2
Hydroxides	$Ce_2O_3 \cdot 6H_2O$	$2CeO_2 \cdot 3H_2O$
Carbonates	$Ce_2(CO_3)_3 + 5H_2O$	$Ce(CO_3)_2 + 0.5H_2O$
Chloride	$CeCl_3$	
Bromide	$CeBr_3$	
Iodide	CeI_3	
Perchlorate	$Ce(ClO_4)_3 + 8H_2O$	
Bromate	$Ce(BrO_3)_3 + 9H_2O$	
Iodate	$Ce(IO_3)_3 + 2H_2O$	
Fluorides	CeF_3	$CeF_4 + H_2O$
Cyanide	$Ce(CN)_3$	
Ferrocyanides	$Ce_4(FeC_6N_6)_3 + 30H_2O$ $CeKFeC_6N_6 + 3H_2O$	
Ferricyanide	$CeFeC_6N_6 + 8H_2O$	
Sulphocyanide	$Ce(CSN)_3 + 7H_2O$	
Sulphide	Ce_2S_3	
Sulphite	$Ce_2(SO_3)_3 + 3H_2O$	
Sulphates	$Ce_2(SO_4)_3 + 3, 5, 6, 8, 9,$ and $12H_2O$	$Ce(SO_4)_2 + 4H_2O$

Double sulphates.	$Ce_2(SO_4)_3 \cdot 3K_2SO_4 + 2H_2O$	$Ce(SO_4)_2 \cdot 2K_2SO_4 + 2H_2O$
	$Ce_2(SO_4)_3 \cdot Na_2SO_4 + 2H_2O$	
	$Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 8H_2O$	
Nitrates.	$Ce(NO_3)_3 + 6H_2O$	$Ce(NO_3)_4$
Double nitrates.	$Ce_2(NO_3)_6 \cdot 3Zn(NO_3)_2 + 24H_2O$	$2Ce(NO_3)_4 \cdot 4KNO_3 + 3H_2O$
	$Ce_2(NO_3)_6 \cdot 3Co(NO_3)_2 + 24H_2O$, etc.	$2Ce(NO_3)_4 \cdot 4(NH_4)NO_3 + 3H_2O$
Phosphates.	$CePO_4$	$(CeO_2)_4 \cdot (P_2O_5)_6 + 26H_2O$
Oxalate.	$Ce_2(C_2O_4)_3$	
Carbide.		CeC_2

B. Characteristics. Cerium exists in compounds in two conditions of oxidation.* The higher or ceric salts are easily reduced to the lower or cerous condition by the ordinary reducing agents (e.g. H_2S, SO_2, $H_2C_2O_4$, etc.), and the cerous salts may be oxidized to the ceric condition by oxidizing agents (e.g. PbO_2+HNO_3, H_2O_2 in alkaline solution, $KMnO_4$, etc.). In general the cerous salts are colorless, and the ceric yellow. The lower oxide of cerium, (Ce_2O_3), on ignition goes over to the higher condition, (CeO_2). The cerous salts are the more stable, and consequently they form the greater number. They resemble the yttrium salts in many of their reactions, and are distinguishable from them chiefly by the greater insolubility of the double sulphates with sodium sulphate and potassium sulphate respectively in excess of the alkali sulphate, by the comparative insolubility of the carbonate in ammonium carbonate, and by the possibility of oxidation to a higher condition. Solutions of pure cerium salts give no absorption bands.

Estimation. *A. Gravimetric.* Cerium is usually determined gravimetrically as the dioxide, (CeO_2), obtained by the ignition of the hydroxide or the oxalate (*vid.* James, Jour. Amer. Chem. Soc. XXXVI, 909).

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* Meloche has prepared derivatives of a perceric oxide (CeO_3), namely, the double carbonate ($Ce_2O_4(CO_3)_2 \cdot 4K_2CO_3 \cdot 12H_2O$) and the acetate (Jour. Amer. Chem. Soc. XXXVII, 2338, 2645).

B. Volumetric. (1) When ceric oxide, (CeO_2), is treated with hydrochloric acid in the presence of potassium iodide, iodine is set free, according to the following equation:

$$2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 4H_2O + 2KCl + I_2.$$

The iodine may be estimated in acid solution by standard thiosulphate, or in alkaline solution by standard arsenious acid (Bunsen, Ann. Chem. Pharm. CV, 49; Browning, Amer. Jour. Sci. [4] VIII, 451).

(2) When cerium oxalate is dissolved in sulphuric acid the oxalic acid may be readily determined by potassium permanganate, and the amount of cerium present may be thus estimated (Stolba, Zeitsch. anal. Chem. XIX, 194; Browning, Amer. Jour. Sci. [4] VIII, 457).

(3) When yellow ceric compounds are treated with hydrogen dioxide in acid solution, they are reduced to cerous compounds, with bleaching of color (Knorre, Zeitsch. angew. Chem. (1897), 685):

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2.$$

(4) Cerium may be estimated in the presence of the other rare earths by precipitating the hydroxide in the presence of potassium ferricyanide, filtering, and estimating by potassium permanganate the ferrocyanide formed (Browning and Palmer, Amer. Jour. Sci. XXVI (1908), 83), according to the equations:

(1) $2K_3FeC_6N_6 + Ce_2O_3 + 2KOH = 2K_4FeC_6N_6 + H_2O + 2CeO_2$.

(2) $5K_4FeC_6N_6 + KMnO_4 + 4H_2SO_4 = 5K_3FeC_6N_6 + 3K_2SO_4 + MnSO_4 + 4H_2O$.

Separation. Cerium falls into the analytical group with aluminum, iron, etc. Together with the other rare earths it may be separated from these by oxalic acid or oxalate of ammonium. For separation from the yttrium earths, *vid.* page 49.

Cerium may be separated from lanthanum, praseodymium, and neodymium by the following methods: (1) by treating the hydroxides suspended in a solution of caustic potash with chlorine gas (Mosander, J. pr. Chem. xxx, 267), or with liquid bromine (Browning and Roberts, Amer. Jour. Sci. xxix, 45); (2) by boiling a solution of the nitrates with potassium bromate in presence of a lump of marble, thus precipitating basic ceric nitrate (James and Pratt, Jour. Amer. Chem. Soc. xxxiii, 1326); (3) by treating a solution of the cerium earths with sodium peroxide and boiling (O. N. Witt, Chem. Ind. (1896), ii, 19); (4) by treating the oxalates of the cerium earths with warm dilute nitric acid, thus separating the cerium as basic nitrate (Auer von Welsbach, Monatshefte f. Chem. v, 508); (5) by treating a solution of the salts with hydrogen dioxide in the presence of magnesium acetate (Meyer and Koss, Ber. Dtsch. chem. Ges. xxxv, 672); (6) by treating the neutralized nitrate solution with an excess of zinc oxide and adding potassium permanganate, thus precipitating cerium peroxide; (7) by the action of chromic acid on the hydroxides, dissolving the cerium (Esposito, Proc. Chem. Soc. xxii, 20).

From thorium cerium may be separated (1) by repeated precipitations on boiling with sodium thiosulphate (Fresenius and Hintz, Zeitsch. anal. Chem. xxxv, 543); (2) by boiling with potassium trinitride (Dennis and Kortright, Amer. Chem. Jour. xvi, 79):

$$Th(NO_3)_4+4KN_3+4H_2O=Th(OH)_4+4KNO_3+4HN_3;$$

(3) by boiling a nearly neutral solution of the chlorides with copper and cuprous oxide (Lecōq de Boisbaudran, Compt. rend. xcix, 525); (4) by the action of fumaric

acid in 40% alcohol upon solutions of the salts in 40% alcohol (Metzger, Jour. Amer. Chem. Soc. XXIV, 901); (5) by oxidizing cerous salts to the ceric condition and treating with ammonium oxalate, cerium not being precipitated at first (Orlow, Chem. Ztg. XXX, 733). In all of these methods the thorium is precipitated. The separation from thorium may be accomplished also by electrolysis of the nitrates (Dennis, U. S. Patent, 1, 115, 513, Nov. 1914).

Cerium is separated from zirconium by fusion of the oxides with acid potassium fluoride, and extraction with water and a little hydrofluoric acid; the potassium fluozirconate is dissolved, and the thorium and cerium remain* (Delafontaine, Chem. News LXXV, 230).

In addition to the foregoing, Methods 1, 3, 4, 6–10, 18, and 26(*b*), page 43, have been used in separating cerium from its associates.

Experimental Work. *Vid.* end of the chapter.

2. **LANTHANUM,** La, 139
3. **PRASEODYMIUM,** Pr, 140.9
4. **NEODYMIUM,** Nd, 144.3
5. **SAMARIUM,** Sm, 150.4
6. **SCANDIUM,**† Sc. 44.1

Discovery. In 1839 Mosander found that when the nitrate of cerium had been ignited, he was able to extract from it by very dilute acid an earth which differed in properties from that of cerium, while from the portion remaining undissolved he obtained the reactions of the cerium earth. He supposed the unknown substance of the newly discovered earth to be an element, and named it Lanthanum, from λανθάνειν, *to hide* (Pogg. Annal. XLVI, 648; Liebig, Annal. XXXII, 235).

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* For the action of organic bases as precipitants of the rare earths, *vid.* Jefferson, Jour. Amer. Chem. Soc. XXIV, 540; Baskerville, Science, New Series, XVI, 215; Kolb, J. pr. Chem. [2] LXVI, 59; Allen, Jour. Amer. Chem Soc. XXV, 421; Holmberg, Chem. Zentr. 1906, II, 1595.

† *Vid.* foot-note, page 35.

In 1841, while engaged in further work upon the extraction of mixtures of cerium and lanthanum oxides by dilute nitric acid, he succeeded in separating from the lanthanum oxide another earth, rosy in color, going over to dark brown on being heated. Reserving for the residual oxide the original name Lanthanum earth, he called the base of the new oxide Didymium, from δίδυμος, *twin*,—a name suggested by its close relationship to lanthanum and its almost invariable occurrence with it (Pogg. Annal. LVI, 503).

In 1885 Auer von Welsbach announced that by long-continued fractional crystallization of the double nitrates of ammonium with lanthanum and didymium in the presence of strong nitric acid, he had separated didymium into two elements (Sitzungsber. d. k. Acad. d. Wiss. (1885) XCII, Heft I, II, 317; Ber. Dtsch. chem. Ges. XVIII, 605). The lanthanum crystallized out first, and afterward the decomposition of the didymium took place. To these new elements he gave the names Praseodymium (*πράσινος*, *leek-green*) and Neodymium (*νέος*, *new*).

In 1878 Delafontaine (Compt. rend. LXXXVII, 559, 632) announced the discovery of Decipium in a North Carolina samarskite.

In 1879 Nilson (Ber. Dtsch. chem. Ges. XII, 554), while engaged in extracting ytterbium from euxenite, separated an earth of much lower atomic weight, the unknown element of which he called Scandium.* The same year Lecoq de Boisbaudran (Compt. rend. LXXXVIII, 323), in the course of an examination of the absorption spectra of the earths separated from samarskite, isolated the earth of another new element, Samarium.

Occurrence. The cerium earths occur closely associated with cerium. The following are some of the chief sources:

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* The discovery of scandium was predicted by Mendeléeff in 1869 and the hypothetical element was named Ekaboron. To it he gave the atomic weight of 44, and he described the properties of several of its compounds.

of lanthanum, cerite, allanite, monazite, bastnaesite, and lanthanite; of praseodymium and neodymium, cerite, allanite, monazite, and bastnaesite; of samarium, samarskite, orthite, cerite, gadolinite, and keilhauite; of scandium, gadolinite, yttrotitanite, euxenite, and keilhauite; of decipium, samarskite.

Extraction. In the process of extracting cerium from cerite (*vid.* Experiment 1) the oxalates of the cerium earths are precipitated together.

The Elements. I. LANTHANUM. *A. Preparation.* The element lanthanum may be obtained (1) by reducing the chloride with potassium; (2) by subjecting the double chloride of lanthanum and sodium to electrolysis.

B. Properties. Lanthanum is a metallic element of a lead-gray color. It decomposes cold water slowly and hot water more rapidly, with the evolution of hydrogen. It oxidizes easily in the air. Its specific gravity is from 6.04 to 6.19, and its melting-point is 810° C.

II. PRASEODYMIUM AND NEODYMIUM. The elements praseodymium and neodymium have been isolated by the electrolysis of the anhydrous chlorides (Muthmann and Weiss, Liebig Ann. CCCXXXI, 46). Their melting-points are 940° C. and 840° C., respectively.

III. SAMARIUM AND SCANDIUM. Samarium has been obtained by the electrolysis of a mixture of samarium and barium chlorides. The melting-point of samarium is 1300°–1400° C. The element scandium seems not to have been isolated.

Compounds. *A. Typical forms.* In the table on the next page are shown typical compounds of the members of the cerium group other than cerium.

B. Characteristics. The compounds of the other members of the cerium group are very similar to those of cerium in the cerous condition in their behavior toward chemical reagents. They may be distinguished from the compounds of cerium by the absence of yellow color on the addition of

Oxides	La_2O_3	Pr_2O_3	Nd_2O_3	Sc_2O_3 *	Sm_2O_3
		Pr_4O_7			Sm_4O_9
		Pr_2O_4			
Hydroxides	$La(OH)_3$			$Sc_2O_3+6H_2O$	$Sm_2O_3+6H_2O$
Chlorides	$LaCl_3+7H_2O$	$PrCl_3+7H_2O$	$NdCl_3+6H_2O$	$Sc_2Cl_6+3H_2O$ & $12H_2O$	$SmCl_3+6H_2O$
Oxychlorides	$LaOCl$				$SmOCl$
Chlorate	$La(ClO_3)_3$				
Perchlorate	$La(ClO_4)_3+9H_2O$				
Bromides	$LaBr_3+7H_2O$	$PrBr_3+6H_2O$		$Sc_2Br_3+3H_2O$ & $12H_2O$	$SmBr_3+6H_2O$
Bromate	$La(BrO_3)_3+9H_2O$				
Iodide					SmI_3
Iodates	$La_2(IO_3)_6+3H_2O$				$Sm(IO_3)_3+6H_2O$
Fluoride					$SmF_3+0.5H_2O$
Sulphides	La_2S_3 †	Pr_2S_3 †	Nd_2S_3		Sm_2S_3
Sulphites	$La_2(SO_3)_3+4H_2O$				$Sm_2(SO_3)_3$
Sulphates	$La_2(SO_4)_3+9H_2O$	$Pr_2(SO_4)_3+8H_2O$	$Nd_2(SO_4)_3+8H_2O$	$Sc_2(SO_4)_3$	$Sm_2(SO_4)_3+8H_2O$
		$Pr_2O_2SO_4$	$Nd_2O_2SO_4$		
		$PrH_3(SO_4)_3$	$NdH_3(SO_4)_3$		
Double sulphates	$La_2(SO_4)_3 \cdot 3K_2SO_4$	$Pr_2(SO_4)_3 \cdot 3K_2SO_4+H_2O$		$Sc_2(SO_4)_3+3K_2SO_4$	$2Sm_2(SO_4)_3+9K_2SO_4$
	$La_2(SO_4)_3 \cdot Na_2SO_4+2H_2O$	$Pr_2(SO_4)_3 \cdot (NH_4)_2SO_4+8H_2O$		$Sc_2(SO_4)_3+3Na_2SO_4$	$Sm_2(SO_4)_3 \cdot Na_2SO_4$
	$La_2(SO_4)_3 \cdot (NH_4)_2SO_4+8H_2O$				$Sm_2(SO_4)_3 \cdot (NH_4)_2SO_4$
Selenites	$La_2(SeO_3)_3+9H_2O$	$Pr_2(SeO_3)_3 \cdot H_2SeO_3+3H_2O$		$Sc_2(SeO_3)_3+H_2O$	
Seleniates	$La_2(SeO_4)_3+6H_2O$	$Pr_2(SeO_4)_3+8H_2O$			$Sm_2(SeO_4)_3+8H_2O$
Double seleniates	$La_2(SeO_4)_3 \cdot K_2SeO_4+9H_2O$	$Pr_2(SeO_4)_3 \cdot K_2SeO_4+4H_2O$			
	$La_2(SeO_4)_3 \cdot Na_2SeO_4+4H_2O$				
	$La_2(SeO_4)_3 \cdot (NH_4)_2SeO_4+9H_2O$				
Nitrates	$La(NO_3)_3+6H_2O$	$Pr(NO_3)_3+6H_2O$	$Nd(NO_3)_3$	$Sc(NO_3)_3$	$Sm(NO_3)_3+6H_2O$
Double nitrates		$Pr(NO_3)_3 \cdot 2(NH_4)NO_3+4H_2O$			
		$Pr(NO_3)_3 \cdot 2NaNO_3+H_2O$			
Phosphates	$LaPO_4$; also meta and pyro forms				$SmPO_4$
Carbonates	$La_2(CO_3)_3+3H_2O$	$Pr_2(CO_3)_3+8H_2O$		$Sc_2(CO_3)_3+12H_2O$	$Sm_2(CO_3)_3+3H_2O$
Oxalates	$La_2(C_2O_4)_3$	$Pr_2(C_2O_4)_3+10H_2O$	$Nd_2(C_2O_4)_3+11H_2O$	$Sc_2(C_2O_4)_3+6H_2O$	$Sm_2(C_2O_4)_3+10H_2O$

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* Crookes (Proc. Roy. Soc. (London), (A) LXXX, 516 and LXXXIV, 79) has prepared a large number of salts of scandium; many of them are salts of organic acids and are basic; *vid.* also Meyer, Ztschr. anorg. Chem. LXXXVI, 257. † Biltz, Ztschr. anorg. Chem. LXXI, 182.

oxidizing agents,—a color characteristic of the higher oxide of cerium. Lanthanum may be distinguished from praseodymium and neodymium by the colorlessness of its salts and by the absence of an absorption spectrum.

Praseodymium salts are green. While their chemical form resembles closely that of the neodymium salts, higher oxides are definitely known in the case of praseodymium. The ordinary oxide Pr_2O_3 is greenish white; the higher oxide Pr_4O_7 is nearly black. Neodymium salts in general are of a rosy color, but the oxide Nd_2O_3 is bluish. Each of the two elements has distinctive spectra, spark and absorption. The lower oxide and the salts of samarium are yellow. Solutions of the salts give characteristic absorption bands. The oxides and salts of scandium are colorless. The salts show no absorption spectrum.

Estimation. Like cerium, the other members of its group are generally estimated as oxides, obtained by ignition of the hydroxides or oxalates.

Separation. *A. Lanthanum from praseodymium and neodymium.* Lanthanum may be separated from praseodymium and neodymium (1) by dissolving the sulphates in water at 9° C. and gradually raising the temperature,—the lanthanum sulphate separating first (Hermann, J. pr. Chem. LXXXII, 385); (2) by heating the nitrates at 400°–500° C. and extracting with water,—praseodymium and neodymium tending to form an insoluble basic nitrate (Damour and Deville, Bull. Soc. Chim. d. Paris, II, 339); (3) by dissolving half of a given amount of the oxides in warm dilute nitric acid, then adding the other half with constant stirring, cooling the mass, and extracting with water (*vid.* Experiment 1), —praseodymium and neodymium being found in the residue (Auer von Welsbach, Monatshefte f. Chem. V, 508); (4) by fractional crystallization of the nitrates with magnesium nitrate,—the lanthanum appearing in the first crystallizations (James, Jour. Amer. Chem. Soc. **XXX**, 979); (5) by treating the hydroxides with bromine water,—the lanthanum being the more soluble (Browning, Compt. rend. CLVIII, 1679).

Separation Methods 1, 9, 11, 12, 17–23, 25(*b*), and 26(*a*), (*b*), and (*c*), page 43, have also been used in separating lanthanum.

B. Praseodymium from neodymium. The separation of praseodymium from neodymium may be accomplished (1) by making several hundred fractional crystallizations, first of the nitrates with ammonium nitrate, and later of the nitrates with sodium nitrate, in the presence of lanthanum and nitric acid,—the neodymium salt being the more soluble (Auer von Welsbach, Sitzungsber. d. k. Acad. d. Wiss. (1885) XCII, Heft I, II, 317); (2) by allowing nitric acid to act upon the oxalates,—the praseodymium salt being the more soluble (Scheele, Ber. Dtsch. chem. Ges. XXXII, 417); (3) by treating the sulphates with water,—the praseodymium sulphate being the more soluble (Muthmann and Rölig, Ber. Dtsch. chem. Ges. XXXI, 1718); (4) by making fractional precipitations of a solution of the nitrates by means of sodium acetate and hydrogen peroxide,—the praseodymium separating first (Meyer and Koss, Ber. Dtsch. chem. Ges. XXXV, 676); (5) by making fractional crystallizations of the nitrates with magnesium nitrate,—the praseodymium appearing first after the lanthanum (*vid.* (4), Separation of Lanthanum from Praseodymium and Neodymium). Methods 1, 8(*a*), 9, 11, 12, 19, 22, 23, and 26(*a*), page 43, have also been used in the separation of praseodymium and neodymium from their associates and from each other.

Samarium, together with gadolinium and europium, is found by James in the mother liquors obtained during the fractionation of the nitrates of lanthanum, praseodymium, and neodymium with magnesium nitrate. Urbain and Lacomb (Compt. rend. CXXXVII, 792, and CXXXVIII, 84) have found that the addition of bismuth-magnesium nitrate helps in the separation. The samarium appears in the least soluble fractions. *Vid.* also Methods 9, 11, 20, 23, and 26(*a*), (*b*), and (*d*), page 43.

Scandium is obtained with ytterbium by James in the mother liquors from the bromate crystallizations (*vid.* diagram, page 216). It is separated from ytterbium by precipitation as the double potassium sulphate. *Vid.* also Methods 8 and 21, page 43.

EXPERIMENTAL WORK ON CERIUM, LANTHANUM, PRASEODYMIUM, AND NEODYMIUM.

Experiment 1. *Extraction of salts of the cerium group from cerite or monazite.* Treat 25 grm. of the powdered mineral with common sulphuric acid and stir until the mass has the consistency of thick paste. Heat until the excess of sulphuric acid is removed. Cool, pulverize, and digest with cold water until no further precipitate appears upon the addition of ammonium oxalate to a few drops of the extract. Pass hydrogen sulphide into the solution to remove traces of bismuth and copper. Filter, and to the filtrate add oxalic acid to complete precipitation of the oxalates of cerium, lanthanum, praseodymium, and neodymium. Ignite the oxalates, and dissolve in hydrochloric acid the oxides obtained. To the solution add potassium hydroxide until the precipitation of the hydroxides is complete. Make up the volume of the liquid in which the hydroxides are suspended to about 200 $cm.^3$ Add about 5 grm. of potassium hydroxide to insure an excess, and pass a slow current of chlorine gas through, stirring from time to time, until the liquid is no longer alkaline in reaction and the precipitate has assumed a deep-yellow color.* By this process the cerium hydroxide is oxidized to the dioxide, which remains undissolved, and the hydroxides of lanthanum, praseodymium, and neodymium are dissolved. When the separation is complete, a portion of the washed precipitate dissolved in hydrochloric acid should give no evidence of the presence of praseodymium or neodymium,—for example, no absorption spectrum (*vid.* Experiment 12). The absence of these elements at this point is considered sufficient evidence of the absence of lanthanum. To the solution containing lanthanum, praseodymium, and neodymium, add oxalic acid until precipitation is complete. Filter off the oxalates, wash, dry, ignite, and set aside for later use the oxides obtained. (For method of separation *vid.* Experiment 13.)

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* The processes of James and Pratt, which use potassium bromate and marble, or of Browning and Roberts, which substitute bromine for chlorine, may be employed for the separation. *Vid.* page 60.

Experiment 2. *Reduction and oxidation of cerium compounds.* (*a*) To a small portion of the carefully washed cerium dioxide obtained in the previous experiment add a little hydrochloric acid diluted with an equal volume of water and boil. Note the evolution of chlorine and the ultimate colorless solution of cerium chloride, ($CeCl_3$).

(*b*) To a portion of the solution obtained in (*a*) add a few drops of ammonium hydroxide in excess and some hydrogen dioxide. Note the orange to red-brown precipitate (CeO_3?). Other oxidizing agents, such as sodium hypochlorite, sodium peroxide, lead dioxide, potassium permanganate, etc., may be used. Boil the solution holding the precipitate in suspension and note that the deep-yellow color changes to a lighter yellow. The precipitate becomes essentially the dioxide, (CeO_2).

(*c*) To another portion of the washed cerium dioxide from Experiment 1 ($2CeO_2 \cdot 3H_2O$) add hydrochloric acid as before, and also a crystal of potassium iodide in the cold. Note the liberation of iodine according to the reaction $2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 2KCl + I_2 + 4H_2O$.

Experiment 3. *Formation of ceric nitrate,* ($Ce(NO_3)_4$). Dissolve in nitric acid a portion of the hydrated ceric oxide formed in Experiment 1. Note the orange-red color.

Try the action of hydrogen dioxide and oxalic acid upon separate portions of the solution.

Experiment 4. *Precipitation of cerous hydroxide*, ($Ce(OH)_3$). (*a*) To a solution of cerium chloride add sodium, potassium, or ammonium hydroxide in solution. Note the insolubility of the hydroxide in excess of these reagents.

(*b*) Repeat the experiment with tartaric acid present in the solution.

Experiment 5. *Precipitation of cerous carbonate*, ($Ce_2(CO_3)_3$). (*a*) To a solution of cerium chloride add a solution of sodium or potassium carbonate. Note the comparative insolubility in excess.

(*b*) Repeat the experiment, using ammonium carbonate as the precipitant.

(*c*) Try the action of the common acids upon the carbonate of cerium.

Experiment 6. *Precipitation of cerium oxalate*, ($Ce_2(C_2O_4)_3$). (*a*) To a solution of a cerium salt add oxalic acid or an oxalate. Note the crystalline character of the precipitate, especially after the liquid has been stirred and boiled.

(*b*) Try the action of hydrochloric acid upon cerium oxalate.

Experiment 7. *Precipitation of the double sulphate of cerium and potassium or sodium*, ($Ce_2(SO_4)_3 \cdot 3K_2SO_4$ or $Ce_2(SO_4)_3 \cdot Na_2SO_4$). To a few drops of a concentrated solution of a cerous salt add a small portion of a saturated solution of sodium or potassium sulphate.

Experiment 8. *Precipitation of cerium phosphate*, ($CePO_4$). (*a*) To a solution of a cerous salt add sodium phosphate in solution.

(*b*) Try the action of hydrochloric and acetic acids upon separate portions of the precipitate.

Experiment 9. *Precipitation of cerous fluoride*, (CeF_3). To a solution of cerium chloride add potassium fluoride in solution.

Experiment 10. *Precipitation of the ferrocyanide of cerium* ($Ce_4(FeC_6N_6)_3$). (*a*) To a solution of cerium chloride add potassium ferrocyanide.

(*b*) Note that potassium ferricyanide gives no precipitate.

Experiment 11. *Comparison of lanthanum, praseodymium, and neodymium with cerium.* (*a*) Perform Experiments 4 to 10 inclusive upon dilute solutions of salts of lanthanum, praseodymium, and neodymium.

(*b*) Note that pure salts of these elements give no change of color with oxidizing agents. Compare with cerium salts (*vid.* Experiment 2).

Experiment 12. *Absorption spectra.* Place solutions of salts of praseodymium and neodymium between the slit of the spectroscope and a luminous flame. Note the dark bands. Observe that cerium and lanthanum salts in solution show no absorption bands.

Experiment 13. *Separation of praseodymium and neodymium.* If time and material allow, an interesting experiment may be performed by taking about 100 grm. of the oxides of lanthanum, praseodymium, and neodymium, dissolving them in a known amount of nitric acid, neutralizing an equal amount of nitric acid by means of magnesium oxide, mixing the two solutions, and proceeding with the fractional crystallization of the double nitrates to the point where change of color indicates the separation of praseodymium and neodymium. Observe the differences in the absorption bands.

Experiment 14. *Negative tests of the salts of cerium, lanthanum, praseodymium, and neodymium.* Note that hydrogen sulphide gives no precipitate with salts of this group. Ammonium sulphide precipitates the hydroxides, not the sulphides.

IV. THORIUM.* Th. 232.4.

Discovery. As early as the year 1818 Berzelius, working on a mineral from Fahlun, Sweden, believed that he had discovered a new earth (Annal. der Phys. u. Chem. (1818) XXIX, 247). He gave it the name Thoria, from Thor, son of the Scandinavian war god Odin. Some years later, however, he identified the supposed new earth as chiefly a basic phosphate of yttrium (Pogg. Annal. IV, 145 . In 1828 Esmark discovered, near Brevig, Norway, the mineral since known as thorite. From it Berzelius isolated an unknown earth; its similarity to the substance described by him some ten years earlier prompted the name Thoria (Pogg. Annal. XVI, 385).

Occurrence. Thorium is found in combination in certain rare minerals (*vid.* Occurrence of Rare Earths, page 35). Its chief sources are monazite, thorianite, and thorite.

Extraction. The following methods may be used for the extraction of thorium salts:

(1) *From thorite.* The mineral is decomposed by heating it with sulphuric acid (*vid.* Cerium, Experiment 1, page 67). After the extraction of the sulphate with cold water, the solution is heated to 100° C. and an impure sulphate of thorium comes down. By repeated solution of the precipitate in cold water and reprecipitation by means of heat a pure sulphate is finally obtained (Delafontaine, Ann. Chem. Pharm. CXXXI, 100).

(2) *From monazite.* (*a*) The mineral is decomposed by sulphuric acid and the oxalates are precipitated by oxalic acid (*vid.* Experiment 1). (*b*) The mineral is heated in an electric furnace with about an equal weight of petroleum coke and very small amounts of lime and fluorspar. The phosphorus distils, the lime is dissolved out by water, the

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* For a discussion of radioactive properties, see Chapter III.

residue is dissolved in hydrochloric acid, and the thorium (ThO_2) is separated by sodium thiosulphate (Baskerville, J. Eng. Ind. Chem. IV, 821).

The Element. *A. Preparation.* Elementary thorium may be obtained (1) by heating the chloride with metallic sodium (Zely and Hamburger); (2) by reducing the double fluoride of potassium and thorium with potassium; (3) by reducing with aluminum.

B. Properties. Thorium is known in two forms, (1) that of a grayish, glistening powder, and (2) crystalline. It is stable in the air, and does not decompose water, even at 100° C. When heated in a current of chlorine, bromine, or iodine, it glows and forms the salt. It is soluble in dilute hydrochloric and sulphuric acids, in concentrated sulphuric acid with the liberation of sulphur dioxide, and in aqua regia. It is acted upon very slowly by nitric acid, and is not attacked by the alkali hydroxides. The specific gravity of thorium in the amorphous condition is 10.97; in crystalline form 11.2.

Compounds. *A. Typical forms.* The following are typical compounds of thorium:

Oxides, ThO_2; Th_2O_7.
Hydroxide, $Th(OH)_4$.
Chlorides, $ThCl_4$; also double salts with KCl and NH_4Cl.
Oxychloride, ThOCl.
Bromide, $ThBr_4$.
Iodide, ThI_4.
Fluoride, ThF_4+4H_2O.
Chlorate, $Th(ClO_3)_4$.
Perchlorate, $Th(ClO_4)_4$.
Bromate, $Th(BrO_3)_4$.
Iodate, $Th(IO_3)_4$.
Sulphide, ThS_2.
Oxysulphide, ThOS.
Sulphite, $Th(SO_3)_2+H_2O$.

Sulphates, $Th(SO_4)_2+9H_2O$; also double salts with K_2SO_4, Na_2SO_4; and $(NH_4)_2SO_4$.
Selenite, $Th(SeO_3)_2+H_2O$.
Seleniate, $Th(SeO_4)_2+9H_2O$.
Nitrate, $Th(NO_3)_4+12H_2O$.
Borides, ThB_4, ThB_6.
Phosphate, $Th_3(PO_4)_4+4H_2O$.
Pyrophosphate, $ThP_2O_7+2H_2O$.
Hypophosphate, ThP_2O_6.
Ferrocyanide, $ThFe(CN)_6+4H_2O$.
Silicide,* ThSi.
Hydride, ThH_4.
Nitride, Th_3N_4.
Carbide, ThC_2.
Silicate, $ThSiO_4$.
Carbonates, $Th(CO_3)_2$; $Th(CO_3)_2 \cdot 3Na_2CO_3+12H_2O$.
Oxalate, $Th(C_2O_4)_2+2H_2O$.

B. Characteristics. The compounds of thorium resemble in chemical form those of cerium in the ceric condition. Thorium resembles cerium also in having a hydroxide insoluble in the alkali hydroxides, and in forming a double sulphate with potassium sulphate, insoluble in excess of that precipitant. The salts of thorium are colorless except where the element is combined with an acid having a color of its own. They are in general insoluble, with the exception of the chloride, the nitrate and the sulphate. Possibly the most distinctive reactions of thorium compounds are the ready formation of a soluble double oxalate when ammonium oxalate is added in excess to a thorium salt in solution, and the precipitation of the hydroxide when a solution of a thorium salt is boiled with potassium hydronitride (Dennis and Kortright, Amer. Chem. Jour. XVI, 79).

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* Hönigschmidt, Compt. rend. CXLII, 157; CXLIII, 224.

Estimation. Thorium is ordinarily estimated as the oxide (ThO_2), obtained by ignition of the hydroxide, the nitrate, or the oxalate.

Separation. Thorium, together with the rare earths cerium, yttrium, zirconium, etc., may be separated from the other elements by oxalic acid. Methods for its separation from yttrium and cerium have already been given (*vid.* pages 49 and 60), but two recent methods may be mentioned here: (1) the action of potassium iodate in the presence of nitric acid upon rare earth solutions,—the thorium salts remaining insoluble even on boiling (R. J. Meyer, Ztsch. f. anorg. Chem. LXXI, 65), a method especially recommended for separations from scandium; (2) the action of sebacic acid on rare earth solutions,—the thorium sebacate being precipitated (Smith and James, Jour. Amer. Chem. Soc. XXXIV, 281).

From zirconium thorium may be separated (1) by the action of acids upon the potassium double sulphates,—the zirconium salt being the more soluble; (2) by the action of an excess of hydrochloric acid upon the soluble double ammonium oxalates,—the zirconium remaining in solution; (3) by fusion with acid potassium fluoride; (4) by the action of dimethylamine upon solutions of the salts,—thorium hydroxide being precipitated (Kolb, J. pr. Chem. [2] LXVI, 59); (5) by electrolysis of the nitrates (Dennis, U. S. Patent 1,115,513, Nov. 1914).

EXPERIMENTAL WORK ON THORIUM.

Experiment 1. *Extraction of thorium oxide from monazite.* Treat 25 grm. of finely ground monazite with common sulphuric acid, according to the method already described (*vid.* Experiment 1, page 67). Precipitate the oxalates with oxalic acid,—not ammonium oxalate,—boil and filter. Remove the oxalates to a porcelain dish, ignite, and dissolve the oxides in nitric acid. Evaporate to dryness to remove excess of acid, dissolve in water, and precipitate thorium thiosulphate with sodium thiosulphate.

Note. This method may be employed for the extraction of thorium from discarded Welsbach-light mantles.

Experiment 2. *Precipitation of thorium hydroxide* ($Th(OH)_4$) *and thorium thiosulphate,*[*] ($Th(S_2O_3)_2$). (*a*) To a solution of a thorium salt add sodium, potassium, or ammonium hydroxide. Note the insolubility of the hydroxide in excess of the precipitant.

(*b*) To a solution of a thorium salt add sodium thiosulphate in solution and boil.

Experiment 3. *Precipitation of thorium carbonate,*[†] ($Th(CO_3)_2$). (*a*) To a solution of a thorium salt add potassium or sodium carbonate. Note the solubility of the precipitate in excess and the reprecipitation on boiling.

(*b*) Repeat, using ammonium carbonate.

(*c*) Note the solvent action of the common acids upon thorium carbonate.

Experiment 4. *Precipitation of the oxalate of thorium,* ($Th(C_2O_4)_2 + 2H_2O$). (*a*) To a solution of a thorium salt add a solution of oxalic acid. Note the insolubility in excess of the precipitant.

(*b*) Repeat, using ammonium oxalate as the precipitant. Note the solubility in excess, especially on warming, and the reprecipitation upon the addition of hydrochloric acid.

(*c*) Try the solvent action of ammonium acetate upon thorium oxalate.

Experiment 5. *Precipitation of the double sulphate of potassium and thorium,* ($Th(SO_4)_2 \cdot 2K_2SO_4 + 2H_2O$ or $Th(SO_4)_2 \cdot 4K_2SO_4 + 2H_2O$). Saturate a solution of a thorium salt with potassium sulphate. (The corresponding sodium salt ($Th(SO_4)_2 \cdot Na_2SO_4 + 6H_2O$) is somewhat soluble in excess of sodium sulphate.)

Experiment 6. *Precipitation of thorium phosphate,*

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[*] According to some authors this precipitate is the hydroxide.

[†] At 50° C. this carbonate is said to become basic.

($Th_3(PO_4)_4+4H_2O$), *and thorium hypophosphate*, (ThP_2O_6). (*a*) To a solution of a thorium salt add sodium phosphate in solution. Orthophosphoric acid is said to precipitate an acid phosphate ($ThH_2(PO_4)_2$). (*b*) To a solution of a thorium salt add sodium hypophosphate in solution. Note the insolubility of the precipitate in fairly strong hydrochloric acid.

Experiment 7. *Precipitation of thorium fluoride*, (ThF_4+4H_2O). To a solution of a thorium salt add a solution of potassium fluoride. Double salts with thorium fluoride may also form ($x KF \cdot y ThF_4$ typical).

Experiment 8. *Precipitation of thorium ferrocyanide*, ($ThFe(CN)_6+4H_2O$). To a solution of a thorium salt add a solution of potassium ferrocyanide. Note the absence of precipitation with potassium ferricyanide.

Experiment 9. *Action of hydrogen peroxide upon salts of thorium.* To a solution of a thorium salt add a little hydrogen peroxide, and warm.

Experiment 10. *Precipitation of thorium iodate*, ($Th(IO_3)_4$). To a solution of thorium nitrate add a solution of potassium iodate. Note the insolubility in fairly strong nitric acid.

Experiment 11. *Precipitation of thorium sebacate.* To a neutral solution of a thorium salt add a hot solution of sebacic acid ($H_2(C_{10}H_{18}O_4)$), and boil.

Experiment 12. *Negative test of thorium salts.* To a solution of a thorium salt add hydrogen sulphide. Note that ammonium sulphide precipitates the hydroxide, not the sulphide.

V. **ZIRCONIUM**, Zr, 90.6.

Discovery. While engaged in the analysis of the zircons, in 1788, Klaproth found one variety containing 31.5% of silica, 0.5% of the oxides of iron and nickel, and 68% of an earth which differed from all earths previously known to him. He observed that it was soluble in the acids, but insoluble in the alkalies, in the latter respect differing from alumina (Ann. de Chim. I, 238). The fact that zircon was the source of the new earth suggested the name Zirconium for the element.

Occurrence. Zirconium is found combined, widely diffused, but always in small quantities (*vid.* Occurrence of Rare Earths, page 35). Its chief source is zircon.

Extraction. Zirconium salts may be extracted from zircon by the following methods:

(1) The finely powdered mineral is fused with acid potassium fluoride (*vid.* Experiment 1) (Marignac, Ann. Chim. Phys. [3] LX, 257).

(2) The mineral is fused with potassium bisulphate and the fused mass extracted with dilute boiling sulphuric acid. The basic sulphate ($3ZrO_2 \cdot SO_3$) is left as a residue (Franz, Ber. Dtsch. chem. Ges. II, 58).

(3) The finely powdered mineral is heated with a mixture of sodium hydroxide and sodium fluoride, the mass is cooled, pulverized, and extracted with water. The residue, which consists mainly of sodium zirconate, is digested with hydrochloric acid until dissolved. After the solution has been evaporated to a small volume the zirconium oxychloride separates in crystalline form (Bailey, Proc. Royal Soc. XLVI, 74).

(4) The finely powdered mineral is fused with sodium carbonate, and the melt, consisting of sodium silicate and sodium zirconate, is extracted with water. The silicate dissolves and the zirconate is hydrolyzed, forming zirconium hydroxide, which, after washing, is dissolved in hydrochloric or sulphuric acid.

The Element.* *A. Preparation.* Elementary zirconium may be obtained in the amorphous condition (1) by reducing potassium fluozirconate with potassium (Berzelius), and (2) by reducing the oxide with magnesium (Phipson). It may be obtained in crystalline form by heating potassium fluozirconate with aluminum (Troost), and in graphitic form by heating sodium fluozirconate with iron at 850° C.

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* *Vid.* Zely and Hamburger, Ztschr. anorg. Chem. LXXXVII, 209.

B. Properties. (1) Zirconium in the amorphous condition is a black powder. Heated in the air it burns brightly to the oxide. It oxidizes also when fused with alkali nitrates, carbonates, and chlorates, and is only slightly attacked by acids.

(2) In crystalline form zirconium has much the appearance of antimony. Heated in the air it oxidizes very slowly. It is not acted upon by fusion with alkali nitrates, carbonates, or chlorates, but is soluble in the acids upon the application of heat. The density of the pure metal is 6.4; its melting-point is 1530° (Wedekind).*

Compounds. *A. Typical forms.* The following are typical compounds of zirconium:

Oxides, ZrO_2; Zr_2O_3; Zr_2O_5.
Hydroxide, $Zr(OH)_4$.
Chlorides, $ZrCl_4$; also double salts with KCl and NaCl.
Oxyhalides, $ZrOCl_2+3H_2O$; $ZrOBr_2+3H_2O$; $ZrI(OH)_3+3H_2O$.
Bromide, $ZrBr_4$.
Iodide, ZrI_4.
Fluoride, ZrF_4.
Oxysulphide, ZrOS.
Sulphite, $Zr(SO_3)_2$.
Sulphates, $Zr(SO_4)_2+4H_2O$; $3ZrO_2 \cdot SO_3$.
Selenite, $Zr(SeO_3)_2$.
Nitrate, $Zr(NO_3)_4+5H_2O$.
Phosphate, $Zr_3(PO_4)_4$.
Pyrophosphate, ZrP_2O_7.
Carbonate, $3ZrO_2 \cdot CO_2+8H_2O$.
Oxalates, $Zr(C_2O_4)_2 \cdot 2Zr(OH)_4$; $Zr(C_2O_4)_2 \cdot K_2C_2O_4 \cdot H_2C_2O_4+8H_2O$.
Zirconates, Na_4ZrO_4; Li_2ZrO_3, etc.

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* U. S. Bureau of Standards gives ±1700° C.

Zirconyl *-nitric or nitrato-zirconic acid, $H_2ZrO(NO_3)_4 + 4H_2O$.

Zirconyl-sulphuric or sulphato-zirconic acid, $H_2ZrO(SO_4)_2 + 3H_2O$.

Fluozirconate, K_2ZrF_6.

Carbide, ZrC.

Silicide, $ZrSi$.

Hydride, ZrH_2.

Nitride, Zr_2N_3.

B. Characteristics. In chemical structure the compounds of zirconium bear a strong resemblance to those of thorium, titanium, germanium, and silicon. The oxide, in its behavior as a base toward oxides having more acidic qualities, resembles the oxide of thorium (ThO_2). With the weaker acids, carbonic and oxalic, it shows weaker basic properties in the formation of basic salts. With strong bases it manifests acidic properties, like the oxide of titanium, and forms zirconates (*vid.* Typical Forms, above). The chief soluble salts are the nitrate and the sulphate. The hydroxide of zirconium is insoluble in excess of the alkali hydroxides, the double sulphate with potassium is insoluble in a solution of potassium sulphate, and the oxalate is soluble in ammonium oxalate. Solutions of pure zirconium salts are said to give no precipitate with hydrofluoric acid or potassium hydronitride. Turmeric paper, when dipped into a solution of a zirconium salt and dried, is colored orange.

Estimation. Zirconium is usually weighed as the oxide (ZrO_2) obtained by ignition of the hydroxide or oxalate.

Separation. Zirconium, with the other rare earths, may be roughly separated from other elements by the action of oxalic acid (*vid.* page 49). For the separation from yttrium, cerium, and thorium see under those elements. The separation of zirconium from iron and titanium has received a good deal of attention from chemists. Some of the methods that have been suggested follow.

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* Rosenheim, Ber. Dtsch. chem. Ges. XL, 803, 810; Hauser, Zeitsch. anorg. Chem. LIII, 74; LIV, 196.

From iron zirconium may be separated (1) by the action of water upon an ethereal solution of the chlorides,—the oxychloride of zirconium being precipitated (Matthews, Jour. Amer. Chem. Soc. XX, 846); (2) by the action of gaseous hydrochloric acid and chlorine at a temperature of about 200° C. upon the mixed oxides,—the ferric chloride being volatilized (Havens and Way, Amer. Jour. Sci. [4] VIII, 217); (3) by treatment with phenylhydrazine,—the zirconium being precipitated (Allen, Jour. Amer. Chem. Soc. XXV, 426); (4) by the action of sulphurous acid on neutral solutions,—the zirconium being precipitated (Baskerville, Jour. Amer. Chem. Soc. XVI, 475).

From titanium zirconium may be separated (1) by boiling a solution containing the two elements with dilute sulphuric and acetic acids,—titanic acid being precipitated free from zirconium (Streit and Franz, J. pr. Chem. CVIII, 75; Zeitsch. anal. Chem. IX, 388); (2) by treating solutions acid with sulphuric or hydrochloric acid with zinc until the titanium is reduced to the condition of the sesquioxide, and then adding potassium sulphate,—the zirconium-potassium sulphate being precipitated (Pisani, Compt. rend. LVII, 298; Chem. News X, 91, 218); (3) by adding hydrogen dioxide and sodium phosphate to the solution,—the basic phosphate of zirconium being precipitated (Hillebrand, Bull. U. S. Geol. Survey No. 176, 75).

EXPERIMENTAL WORK ON ZIRCONIUM.

Experiment 1. Extraction of zirconium salts from zircon. Fuse 5 grm. of finely powdered zircon in a platinum or nickel crucible with about 15 grm. of acid potassium fluoride. Pulverize the fused mass and extract with hot water containing a few drops of hydrofluoric acid.* Filter immediately through a rubber funnel into a rubber beaker. As the filtrate cools, potassium fluozirconate crystallizes out. It may be purified by recrystallization.

Experiment 2. *Precipitation of zirconium hydroxide,* ($Zr(OH)_4$). (*a*) To a solution of a zirconium salt add potassium, sodium, or ammonium hydroxide. Note the insolubility in excess. (*b*) To a solution containing zirconium add sodium thiosulphate in solution and boil.

Experiment 3. *Precipitation of zirconium carbonate,* ($3ZrO_2 \cdot CO_2 + 8H_2O$). (*a*) To a solution of a zirconium salt add sodium or potassium carbonate. Note the partial solubility in excess.

(*b*) Use ammonium carbonate as the precipitant. Note the solvent action of an excess and the precipitation of the hydroxide on boiling.

(*c*) Try the action of the common acids upon separate portions of zirconium carbonate.

Experiment 4. *Precipitation of zirconium oxalate,* ($Zr(C_2O_4)_2 \cdot 2Zr(OH)_4$). (*a*) To a solution of a zirconium salt add a solution of oxalic acid. Note the effect of an excess in the cold and on warming.

(*b*) Use ammonium oxalate as the precipitant. Note the solvent action of an excess and the reprecipitation by ammonium hydroxide.

Experiment 5. *Precipitation of zirconium phosphate,* ($xZrO_2 \cdot yP_2O_5$, *basic*). To a solution of a zirconium salt add sodium phosphate. Orthophosphoric acid precipitates the normal phosphate ($Zr_3(PO_4)_4$).

Experiment 6. *Precipitation of zirconium ferrocyanide,* ($ZrFeC_6N_6$?). To a solution of a zirconium salt add potassium ferrocyanide.

Experiment 7. *Action of zirconium salts upon turmeric paper.* Dip a piece of turmeric paper into a solution of a zirconium salt acidified with hydrochloric acid. Dry on the side of a test-tube or beaker, as in testing for boric acid. Note the yellowish-red color.

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* Glass or porcelain dishes must not be used when hydrofluoric acid is present.

Experiment 8. *Precipitation of zirconium peroxide* (Zr_2O_5). To a solution of a zirconium salt, faintly acidified, add hydrogen dioxide.

Experiment 9. *Negative tests of zirconium salts.* Note that neither hydrogen sulphide nor potassium fluoride gives a precipitate with zirconium salts. Ammonium sulphide precipitates the hydroxide, not the sulphide.

CHAPTER V.

GALLIUM,* Ga, 69.9.

Discovery. In 1875 Lecoq de Boisbaudran, who had done much work with spectrum analysis, notified the Académie des Sciences of his discovery of a new element in a zinc-blende from the mine of Pierrefitte in the Pyrenees, and proposed for it the name Gallium (Compt. rend. LXXXI, 493; Chem. News XXXII, 159). The individuality of the new body was distinctly indicated by the spectroscope, but so small was the amount of it in the possession of the discoverer that few of its reactions were determined. Among the properties which he described, however, were the following: the oxide, or perhaps a subsalt, was thrown down by metallic zinc in a solution containing chlorides and sulphates; in a mixture containing an excess of zinc chloride the new body was the first to be precipitated by ammonia; in the presence of zinc it was concentrated in the first sulphides deposited; the spark spectrum of the concentrated chloride showed two violet lines, one of them of considerable brilliance.

Occurrence. Gallium is found combined, in very small amounts, in certain minerals, chiefly zinc-blendes from Bensberg on the Rhine, Pierrefitte, and other localities. It has been detected in some American zinc-blendes (Chem. Ztg. (1880), 443). The Bensberg sphalerite, one of the richest sources, contains 0.016 grm. per kilo. It has been found also in commercial aluminum and iron (Boulanger and Bardet, Compt. rend. CLVII, 718; Ramage, Chem. News CVIII, 280).

Hartley and Ramage obtained the following interesting results by means of the spectroscope (Jour. London Chem.

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* The discovery of gallium was predicted by Mendeléeff in 1869, and the hypothetical element was named Ekaluminum. It was given the atomic weight of 68, and the specific gravity of 6.

Soc. (1897), 533, 547): the presence of gallium was indicated in thirty-five out of ninety-one iron ores examined; in all the magnetites, seven in number; in all the aluminum ores, fifteen in number, mostly kaolin and bauxite; in four out of twelve manganese ores; and in twelve out of fourteen zinc-blendes.

In 1915 McCutcheon noticed some mercury-like globules upon the surface of a leady residue from the distillation of zinc. Since the residue had been stored away in a warm place, the observer decided to subject it to the action of moist steam. This treatment resulted in a more abundant separation of the peculiar material, which, from the character of its source and its low melting-point, suggested the element gallium. It proved to be essentially an alloy of that element with indium.* Rough analyses of these products showed the gallium-indium alloy to contain about 10 per cent. of indium, with small amounts of zinc and lead, and spectroscopic traces of copper and silver. The leady residue contained about 3 per cent. of gallium and indium together. It also gave spectroscopic evidence of the presence of germanium.†

Extraction. (*a*) Salts of gallium are obtained by the following process: The mineral is dissolved in aqua regia and the excess of acid expelled by boiling. When the solution is cold, pure zinc is added, which precipitates the antimony, arsenic, bismuth, copper, cadmium, gold, lead, mercury, silver, tin, selenium, tellurium, and indium. These are filtered off while there is still some evolution of hydrogen, and the filtrate is boiled from six to twenty-four hours with metallic zinc. Gallium is precipitated as a basic salt, together with salts of aluminum, iron, zinc, etc. To obtain the gallium salt in a more nearly pure condition the precipitate is dissolved in hydrochloric acid, the solution is treated with hydrogen sulphide, and after filtration and the removal of the excess of hydrogen sulphide by boiling, sodium carbonate is added in small portions. The gallium salt is the first to be precipitated, and the precipitates are collected as long as they show the gallium lines in the spark spectrum.* These precipitates are dissolved in sulphuric acid and the solution is diluted largely with water and boiled. The basic sulphate of gallium which is thus thrown down is dissolved in sulphuric acid, and potassium hydroxide is added in excess. Iron if present is removed at this point by filtration and the gallium oxide is then precipitated from the filtrate by carbon dioxide. The discoverer prepared 62 grams of the element from 2400 kilograms of blende. (*b*) Gallium may be obtained from the leady residue from the purification of zinc (*vid.* Experiment 1).

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* Hillebrand and Scherrer, J. Ind. Eng. Chem. VIII, 225; Browning and Uhler, Amer. Jour. Sci. XLI, 351.

† The spectroscopic examination was made by Dr. H. S. Uhler of Yale University.

The Element. *A. Preparation.* Gallium in the elementary condition has been obtained by subjecting an alkaline solution of the oxide to electrolysis.

B. Properties. A gray, lustrous metal, showing greenish-blue lights on reflecting surfaces, gallium is malleable and fairly hard. Its fusing-point, 30.15° C., is so low that it melts readily from the warmth of the hand. In water, and in air at ordinary temperatures, it is unchanged; when heated in air or oxygen it is oxidized only superficially; in fact, it may be heated to redness over a Bunsen burner without appreciable change in weight. It combines rapidly with chlorine, more slowly with bromine, and not at all with iodine unless heat is applied. Gallium is soluble in hydrochloric and warm nitric acids, and somewhat soluble in potash and ammonia solutions. It alloys easily with aluminum, and these alloys decompose cold water rapidly. Its specific gravity is 5.88.

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* Two violet lines, 4172 and 4033.

Compounds. *A. Typical forms.* The following compounds of gallium are known:

Oxides...........	GaO?	Ga_2O_3
Hydroxide.......		$Ga(OH)_3$?
Chlorides........	$GaCl_2$	$GaCl_3$
Bromide.........		$GaBr_3$
Iodide...........		GaI_3
Nitrate..........		$Ga_2(NO_3)_6$
Sulphate.........		$Ga_2(SO_4)_3$
Double sulphate (alum)		$Ga_2(SO_4)_3 \cdot (NH_4)_2SO_4$* $+ 24H_2O$
Ferrocyanide.......		$Ga_4(FeC_6N_6)_3$.

B. Characteristics. The compounds of gallium resemble those of aluminum in forming alums and in having a hydroxide soluble in excess of sodium or potassium hydroxide. The salts are colorless and soluble, and in dilute solutions tend, on being heated, to become basic and separate from the solution. The oxide (Ga_2O_3) is insoluble in acids and alkalies after ignition. Gallium also resembles indium in forming alums, but differs from that element in that its hydroxide is soluble in potassium and sodium hydroxides. Its alums are less soluble in water than those of indium. A very characteristic reaction for gallium is the formation of the ferrocyanide in fairly strong hydrochloric acid. This reaction is useful in separating it from aluminum.†

Estimation. Gallium is usually weighed as the oxide (Ga_2O_3).

Separation.‡ *Vid.* Extraction.

INDIUM, In. 114.8.

Discovery. Indium was discovered by Reich and Richter in 1863, in the course of an examination of two ores consisting mainly of the sulphides of arsenic, zinc, and lead (J. pr. Chem. LXXXIX, 441). These ores had been freed from the greater part of their arsenic and sulphur by roasting, and the residue had been evaporated to dryness with hydrochloric acid and distilled. The crude chloride of zinc thus obtained was examined with the spectroscope for thallium, since the presence of that element had been indicated in similar ores from the Freiberg mines. Instead of the thallium line, however, appeared one of indigo blue never before observed. The color suggested the name Indium for the unknown element present.

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* The cæsium alum forms more readily than the ammonium alum, and seems well adapted for the separation from indium by fractional crystallization, and for the micro-chemical detection.

† Aluminum may be separated from gallium by saturating a solution of the chlorides with HCl gas. $AlCl_3$ is precipitated (Browning and Porter, Amer. Jour. Sci. XLIV, 221).

‡ For a detailed study of the separation of gallium, see many articles by Lecoq de Boisbaudran, Compt. rend. XCIV–XCVIII.

Occurrence. Indium occurs in very small amounts, combined with sulphur, in many zinc-blendes. It has been found in zinc-blende from Freiberg and Breitenbrun in Saxony, and from Schönfeld in Bohemia; in christophite, a variety of zinc-blende; in zinc prepared from these ores; and in the flue-dust from ovens used for roasting zinc ores. It has also been found in wolframite from Zinnwald. The proportion of indium in the minerals named varies from one tenth of one per cent. to mere traces. Lockyer detected it in the atmosphere of the sun. Hartley and Ramage (Jour. London Chem. Soc. (1897), 533, 547) have discovered it spectroscopically in many iron ores,—notably siderites,—in some manganese ores, in zinc-blendes, in five tin ores examined, and in many pyrites.*

Extraction. Indium salts may be obtained as follows from zinc that has been extracted from indium-bearing blendes. The crude metal is nearly dissolved in hydrochloric or nitric acid, and the solution is allowed to stand twenty-four hours with the undissolved metal. A spongy mass, consisting of the indium together with lead, copper, cadmium, tin, arsenic, and iron, collects upon the residual zinc. This mass is washed with water containing some sulphuric acid; it is then dissolved in nitric acid and eva rated with sulphuric acid until all the nitric acid is rem By this process the lead is precipitated, and it may removed by filtration. The solution that remains is trea with ammonium hydroxide in excess, and the hydroxi of iron and indium are filtered off and dissolved in a sm amount of hydrochloric acid. This solution is trea with an excess of acid sodium sulphite and boiled. dium is precipitated as the basic sulphite ($In_2(SO_3)_3 \cdot In_2$ $+5H_2O$). Indium may also be separated from iron treating the chlorides with potassium sulphocyanid extracting the ferric sulphocyanide with ether. may be separated from aluminum and iron by trea the chlorides in alcoholic solution with pyridine. indium is precipitated as a compound of indium chlo and pyridine ($InCl_3 \cdot 3C_5H_5N$) (Dennis, Ber. Dtsch. Ch Ges. XXXVII, 961; Renz, *ibid.* XXXVII, 2110; Mathers, J Amer. Chem. Soc. XXX, 209. *Vid.* also Experiment 1

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* For further discussion of the wide distribution of this element *vid.* Wernadski, Bull. Acad. St. Petersburg (1911), 187 and 1007; Urbain, Compt. rend. CXLIX, 602; Hillebrand and Scherrer, J. Ind. Eng. Chem. VIII, 225.

The Element. *A. Preparation.* Elementary indi may be obtained (1) by heating the oxide with carbon in a current of hydrogen; (2) by heating the oxide w sodium under a layer of dry sodium chloride; (3) by tre ing the salts with zinc; (4) by electrolyzing the sulph in the presence of formic acid (Dennis).

B. Properties. Indium is a soft white metal, less vo tile than cadmium and zinc. It melts at 155° C. (Thi At ordinary temperatures it is stable in the air, but wh heated it ignites and burns with a violet flame to t oxide. It does not decompose boiling water. It dissol easily in hydrochloric, nitric, and sulphuric acids. forms alloys with lead and thallium. Its specific gravi is given at from 7.1 to 7.4.

Compounds.* *A. Typical forms.* The following co pounds of indium are known:

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* The following references will be found helpful: Thiel, Ztsch. anorg. Ch XL, 280; LXVI, 288; Mathers, Jour. Amer. Chem. Soc. XXIX, 485; XXX, 86,

Oxides	InO; In_2O_3
Hydroxide	$In(OH)_3$
Fluoride	$InF_3 + 3H_2O$
Chlorides	$InCl$; $InCl_2$; $InCl_3$
Oxychloride	$InOCl$
Indium - hydrochloric acid	H_3InCl_6
Bromide	$InBr_3$
Iodide	InI_3
Nitrate	$In_2(NO_3)_6 + 9H_2O$
Sulphate	$In_2(SO_4)_3$
Double sulphates	$In_2(SO_4)_3 \cdot K_2SO_4 + 24H_2O$; $In_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 24H_2O$
Sulphite	$In_2(SO_3)_3 \cdot In_2(OH)_6 + 5H_2O$
Sulphides	In_2S; InS; In_2S_3
Sulpho salts	$K_2In_2S_4$; $Na_2In_2S_4$

B. Characteristics. Indium resembles aluminum, iron, and gallium in forming alums, but these alums seem to resemble those of iron more than those of the other elements. It resembles zinc in forming a sulphide with hydrogen sulphide, but in the case of indium this salt is yellow. The hydroxide is insoluble in both sodium and potassium hydroxides, as well as in ammonium hydroxide. Indium monoxide is a dark powder slowly soluble in dilute acids. The sesquioxide is a yellowish-white powder easily soluble in warm acid and more infusible than aluminum oxide. The dichloride is formed directly by the union of chlorine with the metal, and is a white, crystalline mass; in water it separates into the trichloride and the metal. By fusion of the dichloride with elementary indium the monochloride is formed, — a reddish-black, crystalline substance. The trichloride is formed also by the action of chlorine in excess upon the metal; it is white like the dichloride and dissolves in water with the evolution of heat. The nitrate and the sulphate are readily soluble in water and tend to form basic sulphuric acid; it is then dissolved in nitric acid and evaporated with sulphuric acid until all the nitric acid is removed. By this process the lead is precipitated, and it may be removed by filtration. The solution that remains is treated with ammonium hydroxide in excess, and the hydroxides of iron and indium are filtered off and dissolved in a small amount of hydrochloric acid. This solution is treated with an excess of acid sodium sulphite and boiled. Indium is precipitated as the basic sulphite ($In_2(SO_3)_3 \cdot In_2(OH)_6 + 5H_2O$). Indium may also be separated from iron by treating the chlorides with potassium sulphocyanide and extracting the ferric sulphocyanide with ether. Again, it may be separated from aluminum and iron by treating the chlorides in alcoholic solution with pyridine. The indium is precipitated as a compound of indium chloride and pyridine ($InCl_3 \cdot 3C_5H_5N$) (Dennis, Ber. Dtsch. chem. Ges. XXXVII, 961; Renz, *ibid.* XXXVII, 2110; Mathers, Jour. Amer. Chem. Soc. XXX, 209. *Vid.* also Experiment 1).

The Element. *A. Preparation.* Elementary indium may be obtained (1) by heating the oxide with carbon or in a current of hydrogen; (2) by heating the oxide with sodium under a layer of dry sodium chloride; (3) by treating the salts with zinc; (4) by electrolyzing the sulphate in the presence of formic acid (Dennis).

B. Properties. Indium is a soft white metal, less volatile than cadmium and zinc. It melts at 155° C. (Thiel). At ordinary temperatures it is stable in the air, but when heated it ignites and burns with a violet flame to the oxide. It does not decompose boiling water. It dissolves easily in hydrochloric, nitric, and sulphuric acids. It forms alloys with lead and thallium. Its specific gravity is given at from 7.1 to 7.4.

Compounds.* *A. Typical forms.* The following compounds of indium are known:

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* The following references will be found helpful: Thiel, Ztsch. anorg. Chem. XL, 280; LXVI, 288; Mathers, Jour. Amer. Chem. Soc. XXIX, 485; XXX, 86, 211.

Oxides	InO; In_2O_3
Hydroxide	$In(OH)_3$
Fluoride	$InF_3 + 3H_2O$
Chlorides	$InCl$; $InCl_2$; $InCl_3$
Oxychloride	$InOCl$
Indium-hydrochloric acid	H_3InCl_6
Bromide	$InBr_3$
Iodide	InI_3
Nitrate	$In_2(NO_3)_6 + 9H_2O$
Sulphate	$In_2(SO_4)_3$
Double sulphates	$In_2(SO_4)_3 \cdot K_2SO_4 + 24H_2O$; $In_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 24H_2O$
Sulphite	$In_2(SO_3)_3 \cdot In_2(OH)_6 + 5H_2O$
Sulphides	In_2S; InS; In_2S_3
Sulpho salts	$K_2In_2S_4$; $Na_2In_2S_4$

B. Characteristics. Indium resembles aluminum, iron, and gallium in forming alums, but these alums seem to resemble those of iron more than those of the other elements. It resembles zinc in forming a sulphide with hydrogen sulphide, but in the case of indium this salt is yellow. The hydroxide is insoluble in both sodium and potassium hydroxides, as well as in ammonium hydroxide. Indium monoxide is a dark powder slowly soluble in dilute acids. The sesquioxide is a yellowish-white powder easily soluble in warm acid and more infusible than aluminum oxide. The dichloride is formed directly by the union of chlorine with the metal, and is a white, crystalline mass; in water it separates into the trichloride and the metal. By fusion of the dichloride with elementary indium the monochloride is formed, — a reddish-black, crystalline substance. The trichloride is formed also by the action of chlorine in excess upon the metal; it is white like the dichloride and dissolves in water with the evolution of heat. The nitrate and the sulphate are readily soluble in water and tend to form basic salts on being heated. Solutions of indium salts color the flame violet and give a characteristic flame spectrum.

Estimation. Indium is generally determined as the oxide (In_2O_3), obtained by ignition of the hydroxide, or as the sulphide (In_2S_3), obtained by precipitation with hydrogen sulphide in the presence of sodium acetate.

Separation. The separation of this very rare element from those elements with which it is usually associated is treated under extraction.

EXPERIMENTAL WORK ON GALLIUM AND INDIUM.

Experiment 1. *Extraction of indium and gallium from the leady residue from purification of zinc* (approximate composition, Pb 95.6%, In and Ga 3%, Zn 1.2%, Cu traces).

Dissolve the sample in a small amount of a mixture of strong nitric acid and water in equal parts, warming to aid solution. Evaporate to dryness, finishing the evaporation on a steam bath. Treat the dry residue with enough sulphuric acid (1–1) to precipitate lead sulphate completely; warm, filter, and wash with a little sulphuric acid (1–3). To the filtrate add ammonium chloride and ammonium hydroxide to alkalinity, and boil. Filter off indium hydroxide and gallium hydroxide and wash. Dissolve this precipitate in a small amount of hydrochloric acid, evaporate to a few cubic centimeters, and test in the flame and before the spectroscope for indium. To separate gallium treat this solution with a slight excess of sodium hydroxide and warm. Wash the residue, dissolve in hydrochloric acid and test again for indium. To the filtrate add hydrochloric acid to acidity and potassium ferrocyanide. Gallium ferrocyanide is precipitated.

Experiment 2. *Formation of indium hydroxide* ($In(OH)_3$).

(*a*) To a drop of a solution of an indium salt add ammonium chloride and ammonium hydroxide and boil. Note the precipitate of indium hydroxide and its insolubility in excess.

(*b*) To another portion add sodium hydroxide. Note here also the insolubility in excess.

Experiment 3. *Formation of gallium hydroxide* ($Ga(OH)_3$). Repeat the foregoing procedure, using a drop of a solution of a gallium salt instead of the indium. Compare the solubility of gallium hydroxide with that of indium hydroxide in excess of the reagents used.

Experiment 4. *Formation of indium basic sulphite* ($In(OH)SO_3$, typical). To a few drops of a solution of an indium salt add a few drops of a solution of acid ammonium sulphite, and boil.

Experiment 5. *Formation of gallium ferrocyanide* ($Ga_4(FeC_6N_6)_3$. Try the action of potassium ferrocyanide on an acidified solution of a gallium salt. Note precipitate.

Experiment 6. *Spectroscopic test for indium.* Test a solution of an indium salt in the flame, before the spectroscope.

THALLIUM, Tl, 204.

Discovery. Some years previous to 1861 Crookes had been engaged in the extraction of selenium from a seleniferous deposit which he had obtained from the sulphuric-acid manufactory at Tilkerode in the Hartz Mountains. Some residues, left after the purification of the selenium, and supposed to contain tellurium, were set aside and not examined until 1861, when, needing tellurium, Crookes vainly tried to isolate it by various chemical methods. At length he resorted to spectrum analysis and tested some of the residue in the flame. The spectrum of selenium appeared, and as it was fading, and he was looking for evidence of tellurium, a new bright-green line flashed into view. The element whose presence was thus indicated received the name Thallium, from the Greek *θαλλός*, or the Latin *thallus*, *a budding twig* (Chem. News III, 194).

About the same time Lamy announced the discovery of the same element (Ann. Chim. Phys. [3] LXVII, 385);

but after much discussion and the presentation of much evidence on both sides it was declared that Crookes had the priority of discovery.

Occurrence. Thallium occurs in certain very rare minerals:

Crookesite, $(Cu,Tl,Ag)_2Se$, contains 16–19% Tl
Lorandite, $TlAsS_2$, " 59–60% Tl
Hutchinsonite, $(Tl,Ag,Cu)_2S \cdot As_2S_3 + PbS \cdot As_2S_3$, contains 18–25% Tl
Vrbaite, $(TlAs_2SbS_5)$, contains 29–30% Tl.

It is found also in very small quantities in berzelianite, (Cu_2Se); in some zinc-blendes and copper pyrites; in iron pyrites from Theux, Namur, Philippeville, Alais, and Nantes; in lepidolite from Mähren; and in mica from Zinnwald. It has been detected, together with cæsium, rubidium, and potassium, in the mineral waters of Nauheim and Orb. Its presence in the flue-dust from some iron furnaces and sulphuric-acid works, as well as in some crude sulphuric and hydrochloric acids, may be traced to its presence in the pyrites used. It has been found in commercial platinum.

Extraction. Thallium salts may be extracted by the following methods:

(1) *From minerals.* The finely powdered mineral is dissolved in aqua regia. The solution is evaporated with sulphuric acid until the free acid has been removed; it is then diluted abundantly with water, neutralized with sodium carbonate, and treated with potassium cyanide in excess. This precipitates the bismuth and lead, which are filtered off. The filtrate is treated with hydrogen sulphide, which precipitates the cadmium, mercury, and thallium as the sulphides. Very dilute sulphuric acid dissolves the thallium sulphide, leaving the cadmium and mercury sulphides undissolved (Crookes).

(2) *From flue-dust.* The material is treated with an

equal weight of boiling water in a large wooden tub, and is allowed to stand twenty-four hours. The liquid in siphoned off and is precipitated with hydrochloric acid.* The crude chloride thus obtained is treated with an equal weight of sulphuric acid, and heated to expel the hydrochloric acid and the greater part of the excess of sulphuric. The sulphate obtained is dissolved in water, the solution is neutralized with chalk and filtered. By the addition of hydrochloric acid to the filtrate, nearly pure thallous chloride is precipitated (Chem. News VIII, 159).

The Element. *A. Preparation.* The element thallium may be obtained (1) by fusing a mixture of thallous chloride and sodium carbonate with potassium cyanide; (2) by submitting the carbonate or the sulphate to electrolysis; (3) by heating the oxalate; and (4) by precipitating with zinc from an alkaline solution of a thallous salt.

B. Properties. Metallic thallium is in color whitish to blue gray, with the luster of lead. It is soft and malleable and melts at 302° C. It forms alloys with many of the metals (Kurnakow, Zeitsch. anorg. Chem. XXX, 86; LII, 430; Baar, *ibid.* LXX, 352). It oxidizes readily at high temperatures, but is not acted upon by water free from air. It is soluble in dilute nitric and sulphuric acids. It is a poor conductor of electricity. The specific gravity of thallium is 11.88.

Compounds.† *A. Typical forms.* The following are typical compounds of thallium:

Oxides..........	Tl_2O	Tl_2O_3
Hydroxides......	$TlOH$	$Tl(OH)_3$
Carbonate.......	Tl_2CO_3	

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* Three tons of dust gave sixty-eight pounds of crude thallous chloride.

† See also Hawley, Jour. Amer. Chem. Soc. XXIX, 300, 1011; Stortenbeker, Rec. trav. chim. Pays-Bas, XXVI, 248; Thomas, Ann. chim. phys. XI, [8], 204; Franklin, Jour. Amer. Chem. Soc. XXXVII, 2279; Ball, J. Chem. Soc. (London) CIII, 2110, 2130; Buchtala, J. prakt. Chem. [2] LXXXVIII, 771; Beurath, Ztschr. anorg. Chem. XCIII, 161.

Chlorides.........	$TlCl$	$TlCl_3 + H_2O$
Double chlorides ..	$TlCl \cdot HgCl_2$; $3TlCl \cdot FeCl_3$; $TlCl \cdot AuCl_3$; etc.*	$TlCl_3 \cdot 3KCl + 2H_2O$; etc.
Chlorate..........	$TlClO_3$	
Perchlorate.......	$TlClO_4$	
Bromides........	$TlBr$	$TlBr_3$
Double bromides..		$TlBr_3 \cdot KBr + 2H_2O$; $TlBr_3 \cdot 3TlBr$
Bromate.........	$TlBrO_3$	
Iodides..........	TlI	TlI_3
Double iodides....	$TlI \cdot KI$	$TlI_3 \cdot NH_4I$
Iodates..........	$TlIO_3$	$Tl(IO_3)_3$
Periodate........		$3Tl_2O_3 \cdot I_2O_7 + 30H_2O$
Thiosulphate.....	$Tl_2S_2O_3$	
Sulphides........	Tl_2S	Tl_2S_3
Sulphite.........	Tl_2SO_3	
Sulphates........	Tl_2SO_4; $TlHSO_4$	$Tl_2(SO_4)_3$
Double sulphates..	with $MgSO_4$, $ZnSO_4$, $CuSO_4$, etc.	
Alums...........	$Tl_2SO_4 \cdot Al_2(SO_4)_3 + 24H_2O$; $Tl_2SO_4 \cdot Fe_2(SO_4)_3 + 24H_2O$	
Nitrates..........	$TlNO_3$	$Tl(NO_3)_3 + 4H_2O$
Phosphates.......	Tl_3PO_4; $Tl_4P_2O_7$; $TlPO_3$	$TlPO_4 + 2H_2O$
Arseniates........	Tl_3AsO_4	$TlAsO_4 + 2H_2O$
Cyanides.........	$TlCN$	$Tl(CN)_3 \cdot TlCN$
Sulphocyanide....	$TlSCN$	
Ferrocyanide.....	$Tl_4Fe(CN)_6 + 2H_2O$	
Silicofluoride.....	Tl_2SiF_6	
Chromates........	Tl_2CrO_4; $Tl_2Cr_2O_7$	
Chloroplatinate...	Tl_2PtCl_6	
Molybdate........	Tl_2MoO_4	
Tungstate........	Tl_2WO_4	
Vanadates........	Tl_3VO_4; $Tl_4V_2O_7$; $TlVO_3$	

B. Characteristics. Thallium compounds are known in two conditions of oxidation, the thallous, (Tl_2O), and the thallic, (Tl_2O_3). The lower condition is the more stable; consequently the thallous compounds are the more numerous and the better known. When the metal is allowed to oxidize in the air it forms the thallous oxide, but when it is melted in an atmosphere of oxygen, thallic oxide is obtained. Thallic chloride, bromide, and iodide may be formed by treating the corresponding thallous salts with an excess of chlorine, bromine, and iodine, respectively. In general, the thallous salts may be oxidized to the thallic form by strong oxidizing agents, such as potassium permanganate, lead dioxide, barium dioxide, etc. Thallium in the lower condition resembles the alkalies potassium, cæsium, and rubidium in having a soluble hydroxide, carbonate, and sulphate, and an insoluble chloroplatinate and cobaltic nitrite; also in forming alums. It resembles lead in forming an insoluble sulphide and chromate, and in having halogen salts difficultly soluble in cold water but readily soluble in hot water. The thallous salts are colorless when the base is combined with a colorless acid. The sulphide is brownish black. The thallic salts are in general unstable, and on being heated with water tend to precipitate the oxide ($Tl_2O_3 \cdot H_2O$). They may be easily reduced to the lower condition by the action of reducing agents. They may be formed by the careful treatment of thallic oxide with acids as well as by the action of strong oxidizing agents upon the thallous salts. Thallic hydroxide is insoluble, and resembles ferric hydroxide in color. The halogen salts, the nitrate and the sulphate of thallium in the thallic condition are soluble. Solutions of thallium salts in either condition of oxidation give to the flame a characteristic green color.

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* *Vid.* also Korreng, Chem. Zentr. (1914) 1, 610.

Estimation.* *A. Gravimetric.* Thallium is generally weighed in the thallous condition (1) as the chloroplatinate, (Tl_2PtCl_6), after precipitation by chloroplatinic acid (Crookes, Select Methods, Second Edition, 380); (2) as the iodide (TlI), after precipitation by potassium iodide (Werther, Zeitsch. anal. Chem. III, 1, and J. B. (1864), 712; Long, Zeitsch. anal. Chem. XXX, 342); (3) as the chromate (Tl_2CrO_4), after precipitation in alkaline solution by potassium chromate (Browning and Hutchins, Amer. Jour. Sci. [4] VIII, 460); (4) as the sulphate (Tl_2SO_4), after evaporation of appropriate salts with sulphuric acid in excess and ignition at low red heat, or as the acid sulphate, ($TlHSO_4$), obtained by substituting for ignition heating at 220°–240° C. (Browning, Amer. Jour. Sci. [4] IX, 137). It may be estimated also by weighing the gold precipitated according to the equation: $3TlCl + 2AuBr_3 = 2Au + 3TlClBr_2$ (Thomas, Ann. chim. phys. XI [8], 204).

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* See also Hebberling, Liebig Annal. CXXXV, 207; Phipson, Compt. rend. XXVIII, 563; Neumann, Liebig Annal. CCXLIV, 349; Feit, Zeitsch. anal. Chem. XXVIII, 314; Carnot, Compt. rend. CIX, 177; Sponholz, Zeitsch. anal. Chem. XXXI, 519; Thomas, Compt. rend. CXXX, 1316; Marshall, Jour. Soc. Chem. Ind. XIX, 994

B. Volumetric. Thallium is estimated volumetrically (1) by the oxidation of thallous salts with permanganate (Crookes, Select Methods, Second Edition, 381); (2) by the action of potassium iodide upon thallic salts, as shown in the following equation (Thomas, Compt. rend. CXXXIV, 655): $TlCl_3 + 3KI = TlI + 3KCl_3 + I_2$.

Separation.* In the more stable thallous condition, to which thallic salts may readily be reduced, thallium may be separated as follows: from the metals which give precipitates with hydrogen sulphide in acid (but not acetic) solution, by hydrogen sulphide; from elements which form insoluble hydroxides with the alkali hydroxides, by these reagents; and from the alkalies and alkali earths, by ammonium sulphide.

EXPERIMENTAL WORK ON THALLIUM.

Experiment 1. *Extraction of thallium salts from flue-dust.* The method described under Extraction may be followed.

Experiment 2. *Precipitation of thallous chloride, bromide, and iodide* (TlCl; TlBr; TlI). (*a*) To a solution of a thallous salt add hydrochloric acid or a chloride in solution. Note the solvent action of boiling water. Try the effect of cooling the hot solution.

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* See Crookes, Select Methods, Second Edition, 382–386.

(*b*) Repeat the experiment, using potassium bromide as the precipitant.

(*c*) Try similarly potassium iodide.

Experiment 3. *Precipitation of thallium chloroplatinate* (Tl_2PtCl_6). To a solution of a thallous salt add a few drops of a solution of chloroplatinic acid.

Experiment 4. *Precipitation of thallium cobaltic nitrite.* To a solution of a thallous salt add a few drops of a solution of sodium cobaltic nitrite.

Experiment 5. *Precipitation of thallous chromate* (Tl_2CrO_4). To a solution of a thallous salt add some potassium chromate in solution. Try the action of acids upon the precipitate.

Experiment 6. *Precipitation of thallous sulphide* (Tl_2S). (*a*) Through a solution of a thallous salt acidified with dilute sulphuric acid pass hydrogen sulphide. Note the absence of precipitation. Divide the solution, and to one part add ammonium acetate and to the other ammonium hydroxide.

(*b*) Try the action of ammonium sulphide upon a thallous salt in solution.

Experiment 7. *Oxidation of thallous salts.* (*a*) To a solution of a thallous salt acidified with sulphuric acid add gradually a little potassium permanganate. Note the disappearance of the color of the permanganate.

(*b*) To a solution of a thallous salt add bromine water until the color of the bromine ceases to fade. To one portion add a few drops of a solution of a chloride or bromide. Note the absence of precipitation. To another portion add sodium or potassium hydroxide. Note the precipitation of brown thallic hydroxide, ($Tl_2O_3 \cdot H_2O$).

Experiment 8. *Reduction of a thallic salt.* To a solution of a thallic salt formed, for example, as in Experiment 7 (*b*) add stannous chloride. Note the precipitation of thallous chloride (TlCl).

Experiment 9. *Flame and spectroscopic tests for thallium salts.* (*a*) Dip the end of a platinum wire into a solution of a thallium salt and hold it in the flame of a Bunsen burner. Note the green color.

(*b*) Examine spectroscopically the flame colored by a solution of a thallium salt. Observe the green line.

Experiment 10. *Negative tests of thallous salts.* Note that sulphuric acid and the alkali hydroxides and carbonates give no precipitate with solutions of thallous salts.

CHAPTER VI.

TITANIUM, Ti, 48.1.

Discovery. In the year 1791 McGregor (Crell Annal. (1791) I, 40, 103) discovered a new "metal" in a magnetic sand found in Menachan, Cornwall. This sand he named Menachinite, and the newly discovered element Menachite. Four years later Klaproth announced the discovery of a new earth in a rutile which he was engaged in studying (Klapr. Beitr. I, 233). To the metal of this earth he gave the name Titanium, in allusion to the Titans. In 1797, however, he found that titanium was identical with menachite (Klapr. Beitr. II, 236).

Occurrence. Titanium is found combined in many minerals, but never in considerable quantity in any one locality.

	Contains TiO_2
Rutile, TiO_2	90–100%
Dicksbergite, *vid.* Rutile	90–100%
Brookite, TiO_2	90–100%
Octahedrite, TiO_2	90–100%
Pseudobrookite, $Fe_4(TiO_4)_3$	44– 53%
Perofskite, $CaTiO_3$	58– 59%
Ilmenite, $FeTiO_3$	3– 59%
Magnetite, $FeO \cdot Fe_2O_3$	0– 6%
Bauxite, $Al_2O_3 \cdot 2H_2O$	0–4.5%
Geikielite, $MgO \cdot TiO_2$	67– 68%
Senaite, $(Fe,Pb)O \cdot 2(Ti,Mn)O_2$	57– 58%
Uhligite, $Ca(Ti,Zr)O_5 \cdot Al(Ti,Al)O_5$	48– 49%
Arizonite, $Fe_2Ti_3O_9$	56– 57%
Molengraaffite, titanosilicate	27– 28%

Zirkelite, $(Ca,Fe)O \cdot 2(Zr,Ti,Th)O_2$.	14– 15%
Knopite, $RO \cdot TiO_2$	54– 59%
Derbylite, $6FeO \cdot 5TiO_2 \cdot Sb_2O_5$.	34– 35%
Lewisite, $5CaO \cdot 2TiO_2 \cdot 3Sb_2O_5$.	11– 12%
Mauzeliite, $4(Ca,Pb)O \cdot TiO_2 \cdot 2Sb_2O_5$.	7– 8%
Titanite, $CaTiSiO_5$.	34– 42%
Neptunite, $\overset{I}{R}_2\overset{II}{R}TiSi_4O_{12}$.	17– 18%
Keilhauite, complex silicate	26– 36%
Schlormenite, $3CaO(Fe,Ti)_2O_3 \cdot 3(Si,Ti)O_2$	12– 22%
Guarinite, $CaTiSiO_5$	33– 34%
Tscheffkinite, complex silicates	16– 21%
Astrophyllite, $(Na,K)_4(Fe,Mn)_4Ti(SiO_4)_4$	7– 14%
Leucosphenite, $Na_4Ba(TiO)_2(Si_2O_5)_5$	13– 14%
Johnstrupite, complex silicates	7– 8%
Mosandrite, “ “	5– 10%
Rhönite, “ “	9– 10%
Rinkite, “ “	13– 14%
Narsarsukite, “ “	14%
Benitoite, $BaTiSi_3O_9$	20%
Lorenzenite, $Na_2(TiO)_2Si_2O_7$	35%
Delorenzite, complex	66%
Dysanalyte, $6(Ca,Fe)TiO_3 \cdot (Ca,Fe)Nb_2O_6$.	40– 59%
Pyrochlore, $RNb_2O_6 \cdot R(Ti,Th)O_3$,	5– 14%
Æschynite, $\overset{III}{R}_2Nb_4O_{13} \cdot \overset{III}{R}_2(Ti,Th)_5O_{13}$.	21– 22%
Polymignite, $5RTiO_3 \cdot 5RZrO_3 \cdot R(Nb,Ta)_2O_6$.	18– 19%
Yttrocrasite, complex titanite.	49– 50%
Marignacite, *vid.* Pyrochlore	2– 3%
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$.	20– 23%
Polycrase, $\overset{III}{R}(NbO_3)_3 \cdot 2\overset{III}{R}(TiO_3)_3 \cdot 3H_2O$.	25– 29%
Blomstrandite, complex.	10– 19%
Yttrotitanite *vid.* Keilhauite.	

Titanium has been found also in sand on the banks of the North Sea. in some mineral waters, in certain varieties of

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coal, in meteorites, and by means of the spectroscope it has been detected in the atmosphere of the sun. It has been found in the ash of oak, apple, and pear wood, in cow peas, in cotton-seed meal, and in the bones of men and animals. *Vid.* also Baskerville, Jour. Amer. Chem. Soc. XXI, 1099.

Extraction. Titanium salts may be extracted from rutile by the following methods:

(1) The mineral is fused with three parts of a mixture of sodium and potassium carbonates and the fused mass is extracted with water. The titanium, as a sodium or potassium titanate, remains, together with some tin and iron, in the insoluble residue. This mass is treated with strong hydrochloric acid until dissolved. The solution is then diluted, and the tin is removed by hydrogen sulphide. The sulphide of tin is filtered off, the filtrate is made ammoniacal with ammonium hydroxide and again treated with hydrogen sulphide. The iron is precipitated as the sulphide, and the titanium as the hydroxide. After filtration the precipitate is suspended in water and a current of sulphur dioxide is passed through until the black sulphide of iron has dissolved, leaving the oxide of titanium.

(2) The mineral is fused with three parts of acid potassium fluoride and the fused mass is extracted with hot water and a little hydrofluoric acid. The titanium separates, on cooling, as the potassium fluotitanate ($K_2TiF_6 + H_2O$).

(3) The mineral, finely pulverized, is fused with three times its weight of sodium dioxide and the melt is extracted with water. The titanium remains in solution (H. D. Newton).

(4) The mineral is fused with six parts of acid potassium sulphate (*vid.* Experiment 1).

(5) The mineral is mixed with carbon and heated in the electric furnace.* The carbide thus formed is con-

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* The mineral ilmenite may be mixed with sodium sulphate and carbon and heated in an electric furnace (Rossi and Barton, U. S. Patent 1,171,542, Feb. 1916.)

verted into the chloride by heating it with dry chlorine (Stähler, Ber. Dtsch. chem. Ges. XXXVIII, 2619).

(6) The mineral is heated to 1000° and chilled in water. The powder is mixed with aluminum (one-half its weight) and ignited by burning magnesium. On heating the metal obtained to a red heat in a current of dry chlorine titanium tetrachloride distils (Ellis, Chem. News, XCV, 122).

The Element. *A. Preparation.* Elementary titanium may be obtained (1) by heating potassium fluotitanate with potassium (Berzelius and Wöhler); (2) by heating the chloride ($TiCl_4$) in a bomb with metallic sodium (Hunter, Jour. Amer. Chem. Soc. XXXII, 330). *Vid.* also Weiss, Zeitsch. anorg. Chem. LXV, 345; Zely and Hamburger, *ibid.* LXXXVII, 209.

B. Properties. As prepared by Hunter, titanium resembles polished steel. It is quite brittle when cold and readily malleable at low red heat. It does not decompose water at ordinary temperatures and acts on heated water but slightly. When heated in the air it combines with the oxygen, burning brightly to the oxide (TiO_2); in oxygen the combination is accompanied with brilliant light. Titanium is readily soluble in warm hydrochloric acid, and is attacked by dilute hydrofluoric, nitric, sulphuric, and acetic acids. It combines with chlorine. It combines also with nitrogen, forming nitrides. It melts at 1794° C. (Burgess), and its specific gravity is 4.5. It forms alloys with many elements.

Compounds. *A. Typical forms.* The following are typical compounds of titanium:

Oxides...	TiO;	(Ti_3O_4);	Ti_2O_3;	(Ti_7O_{12});	TiO_2;	(Ti_2O_5);	TiO_3
Hydroxides					$Ti(OH)_4$*		$Ti(OH)_6$
Chlorides ..			$TiCl_3$		$TiCl_4$		
Bromide...					$TiBr_4$		
Iodide.....					TiI_4		

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* Orthotitanic acid.

Fluoride...		TiF_4
Titanofluorides.....		$\overset{I}{R}_2TiF_6$, etc.
Sulphides..	Ti_2S_3	TiS_2
Sulphates..	$Ti_2(SO_4)_3$	$Ti(SO_4)_2$
Nitrides *..		Ti_3N_4; Ti_5N_6; TiN_2
Carbide ...		TiC
Silicide....		TiSi
Titanates (meta)		$\overset{II}{R}TiO_3$; $\overset{I}{R}_2TiO_3$
Acids (*vid.* Hydroxides) ...		H_2TiO_3

B. Characteristics. Although a number of oxides of titanium are known, the dioxide is the form generally found, and the salts of that type are by far the most numerous and important. The oxide (TiO_2) resembles the oxide of zirconium (ZrO_2) in acting as a weak base. It forms salts with the strong acids, but does not combine with the weak acids. It unites with the strong bases to form titanates, ($\overset{II}{R}TiO_3$ and $\overset{I}{R}_2TiO_3$). It has less basic and more acidic properties than the oxide of zirconium. The tetrachloride is a colorless liquid which fumes in the air. Practically all the salts of titanium are insoluble in water, the presence of free acid being necessary to prevent the formation of insoluble basic compounds. Titanium, in its behavior toward reagents, resembles quite closely both niobium and tantalum, with which it is often found associated (*vid.* Occurrence).

Estimation.† *A. Gravimetric.* Titanium is usually precipitated as the acid, either by ammonium hydroxide or by boiling a dilute solution acidified with acetic or sulphuric acid; the precipitate is ignited and the element is determined as the oxide (TiO_2).

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* *Vid.* Ruff, Ber. Dtsch. chem. Ges. XLV, 1364, for recent work on nitrides and ammono compounds.

† For estimation in ores, see Technical Methods of Ore Analysis, Low, John Wiley & Sons, New York, 1906.

*B. Volumetric.** Titanium is estimated volumetrically (1) by treating with hydrogen dioxide a definite amount of the titanium solution to be determined and comparing its color with that of a definite amount of a standard solution of titanium similarly treated (Weller, Ber. Dtsch. chem. Ges. xv, 2592); (2) by reducing the titanium from the dioxide to the sesquioxide condition, by the use of zinc and hydrochloric acid, and then oxidizing it with permanganate (Osborn, Amer. Jour. Sci. [3] xxx, 329); (3) by reducing the titanium from the dioxide to the sesquioxide condition in an atmosphere of hydrogen, by means of zinc and sulphuric acid, then oxidizing it by an excess of ferric salt, and estimating the titanium originally present by titrating with potassium permanganate the ferrous salt formed (Newton, Amer. Jour. Sci. xxv (1908), 130).

Separation. The general method for the separation of titanium from the other members of the aluminum group is to boil dilute acidified solutions (*vid.* Gravimetric Estimation). The titanium precipitate, however, carries down traces of other elements, as aluminum and iron.

From iron titanium may be separated (1) by passing hydrogen sulphide into an alkaline solution to which ammonium tartrate has been added,—the iron sulphide being precipitated (Gooch, Amer. Chem. Jour. VII, 283); (2) by treating a mixture of ferrous sulphide and titanic acid with sulphur dioxide (*vid.* Extraction); (3) by boiling a neutral solution with hydrogen dioxide,—metatitanic acid being precipitated; (4) by shaking a solution of the chlorides with ether, the ferric chloride dissolving.

From aluminum titanium may be separated by boiling a solution containing them, in the presence of an alkali acetate and of acetic acid to about seven per cent. of the whole solution,—titanium basic acetate being precipitated (Gooch, Amer. Chem. Jour. VII, 283).

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* *Vid.* also van Brunt, Jour. Amer. Chem. Soc. XXXVI, 1426; Knecht and Neumann, Ztschr. angew. Chem. XXVI, 613, 734; XXVII, 56; McCabe, J. Ind. Eng. Chem. v, 735.

From both iron and aluminum titanium may be separated by precipitation with "cupferron" (Thornton, Amer. Jour. Sci. [4] XXXVII, 407; Bellucci, Gazz. chim. ital. XLIII, I, 570). It may also be separated from these elements as the phosphate in acid solution (Jamieson and Wrenshall, J. Ind. Eng. Chem. VI, 203).

From cerium and thorium titanium may be separated by precipitating the double sulphates of those elements with potassium sulphate. Methods for the separation from zirconium have already been given (*vid.* Zirconium). From niobium and tantalum titanium may be separated* by repeated fusions with acid potassium sulphate and extractions of the melt with water,—the titanium being in soluble form. A satisfactory separation of niobium from titanium may be effected by crystallizing the niobium-potassium oxyfluoride from 35% hydrofluoric acid. The titanium remains in solution (C. W. Balke and E. F. Smith, Jour. Amer. Chem. Soc. XXX, 1637).

EXPERIMENTAL WORK ON TITANIUM.

Experiment 1. *Extraction of titanium salts from rutile.* (*a*) Mix 5 grm. of finely powdered mineral with about 30 grm. of acid potassium sulphate and fuse until the mass is free from black particles. Pulverize the fused mass and extract with cold water, stirring frequently until solution is complete. Filter, and to the filtrate add ammonium sulphide, filter and wash. Suspend the precipitate, which consists mainly of titanium hydroxide and ferrous sulphide, in water, and pass a current of sulphur dioxide through the liquid, or add a solution of ammonium bisulphite, until the ferrous sulphide has dissolved, as shown by the disappearance of the dark color. Filter, and wash the titanium hydroxide which remains.

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* E. F. Smith, Proc. Amer. Philos. Soc. XLIV (1905), 151, 177.

(*b*) *Alternative method.* After having dissolved the fused mass in cold water (*vid.* (*a*)) add about 20 grm. of tartaric acid and make the solution faintly ammoniacal. Pass hydrogen sulphide until the iron is completely precipitated. Filter, add about 10 cm.^{3} of concentrated sulphuric acid to the filtrate, and evaporate in a porcelain dish under a draught hood until the tartaric acid is thoroughly carbonized. Allow the mass to stand until cool, add water, keeping the liquid cool to prevent the precipitation of the titanium hydroxide, and decant from the carbon residue. Filter the brown liquid through animal charcoal previously freed from phosphates, and precipitate the titanium hydroxide with ammonium hydroxide (R. G. Van Name). The tartaric acid may be decomposed by fuming nitric acid and the titanium quantitatively determined (W. M. Thornton, Amer. Jour. Sci. XXXIV, 214).

Experiment 2. *Precipitation of titanium hydroxide*, ($Ti(OH)_4$). (*a*) To a solution containing titanium add sodium, potassium, or ammonium hydroxide. Note the comparative insolubility in excess, especially in ammonium hydroxide. Repeat, having hydrogen dioxide present in the solution.

(*b*) Repeat the experiment, using the alkali carbonates. The precipitate is the same as in (*a*).

(*c*) Note the solubility of the freshly precipitated hydroxide in the common acids.

(*d*) Ignite a portion of the precipitate and try its solubility in acids.

Experiment 3. *Precipitation of titanic hydroxide or acid by boiling.* (*a*) Boil a dilute acid solution of titanic hydroxide. Note the precipitation. Filter, and test the filtrate with ammonium hydroxide.

(*b*) To a solution of titanic acid containing enough free acid to prevent precipitation on boiling, add ammonium acetate. Try similarly sodium thiosulphate.

Experiment 4. *Precipitation of basic titanic phosphate*,

($Ti(OH)PO_4$). To a solution containing titanic acid add a little sodium phosphate in solution. Repeat, having hydrogen dioxide present in the solution.

Experiment 5. *Color tests of solutions containing titanium.* (*a*) To an acid solution containing titanium add hydrogen dioxide. Note the yellow color (TiO_3 in solution).

(*b*) To a solution containing titanium add a piece of metallic zinc and enough acid to start the action. Note the violet color which develops.

Experiment 6. *Negative test of titanium compounds.* Pass hydrogen sulphide through a solution containing titanium. Note the absence of precipitation.

GERMANIUM,* Ge, 72.5.

Discovery. In 1886 Clemens Winkler announced the presence of a new element in the silver mineral argyrodite, which had been discovered the previous year by Weisbach, in the Himmelsfürst mine near Freiberg (Ber. Dtsch. chem. Ges. XIX, 210). According to Winkler's analysis of argyrodite, the sum of its component parts was seven per cent. less than it should have been; and although he repeated the analysis several times with great care, the outcome was always the same. This uniformity of result forced upon him the conclusion that an unknown element was probably present; and after much careful and patient work he was successful in isolating it and investigating its properties. On heating the mineral out of contact with the air, he obtained a dark-brown fusible sublimate, which proved to be chiefly two sulphides, that of the new element, named by him Germanium, and the sulphide of mercury.

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* The discovery of this element was predicted by Mendeléeff in 1869 and the hypothetical element was named Ekasilicon. It was given an atomic weight of 72, and a specific gravity of 5.5. Its oxide, chloride, ethide, and fluoride, as described by Mendeléeff, resemble closely the corresponding compounds of Ge.

Occurrence. Germanium is found in combination in a few rare minerals.

	Contains Ge
Argyrodite, $4Ag_2S \cdot GeS_2$	6–7%
Canfieldite, $4Ag_2S \cdot (Ge,Sn)S_2$	1.82%
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$	traces

It occurs also in some zinc-blendes (Urbain,* Compt. rend. CXLIX, 602; CL, 1758). It has recently been found in a sulphide from Missouri, and in a blende from Wisconsin (Buchanan, J. Ind. Eng. Chem. VIII, 585).

Bardet * has found evidence of its presence in a number of French mineral waters (Compt. rend. CLVII, 224). Uhler has found it to be present also in the "leady residue" from which gallium and indium have been extracted (*vid.* page 84).

Extraction. Germanium salts have been extracted as follows:

(1) A Hessian crucible is heated to redness, and small quantities of a mixture consisting of three parts of sodium carbonate, six parts of potassium nitrate, and five parts of argyrodite are gradually put in. After being heated for some time the molten mass is poured into an iron dish and allowed to cool. The salt mass may then be removed from the silver, pulverized, and extracted with water. The extract is treated with sulphuric acid and evaporated until all the nitric acid is driven off. The residue is dissolved in water and allowed to stand until the oxide of germanium separates from the solution.

(2) Treat the finely powdered zinc-blende with strong sulphuric acid, and evaporate to dryness. Dissolve in water and add sodium sulphide. Treat the sulphide with sulphuric acid (15 : 100). The sulphide of germanium

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* Urbain obtained 5 grm. of germanium from 550 kilos of a Mexican blende and Bardet 0.06 grm. of GeO_2 from 250,000 liters of Vichy mineral water.

remains, and the sulphide of zinc dissolves (Urbain, Compt. rend. CL, 1758; *vid.* also Bardet, *ibid.* CLVIII, 1278).

(3) The substance containing germanium is dissolved in strong hydrochloric acid, and the solution is distilled to about one-half its volume in a current of chlorine,* a condition necessary to keep the arsenic in the higher condition of oxidation. The germanium is in the distillate, and may be precipitated from this by hydrogen sulphide in the presence of strong hydrochloric acid (Buchanan, J. Ind. Eng. Chem. VIII, 585).

The Element. *A. Preparation.* Elementary germanium may be obtained (1) by heating the oxide with carbon; (2) by heating the oxide in a current of hydrogen.

B. Properties. Germanium is a grayish-white, metallic element, having a fine luster, and crystallizing in regular octahedra. It volatilizes slightly when heated in hydrogen or nitrogen at about 1350° C.; its melting-point is about 900° C. In the air it does not oxidize at ordinary temperatures, but when heated goes over to the oxide GeO_2. It is not attacked by dilute hydrochloric acid, is oxidized by nitric acid, and is dissolved by aqua regia. It is dissolved also by sulphuric acid, with the evolution of sulphur dioxide. It combines directly with chlorine, bromine, and iodine. Its specific gravity is 5.46.

Compounds. *A. Typical forms.* The following are typical compounds of germanium:

Oxides	GeO	GeO_2
Chlorides	$GeCl_2$	$GeCl_4$
Oxychloride		$GeOCl_2$
Bromide		$GeBr_4$
Iodide		GeI_4
Fluoride		GeF_4; K_2GeF_6; H_2GeF_6
Sulphides	GeS	GeS_2
Chloroform		$GeHCl_3$
Ethyl		$Ge(C_2H_5)_4$

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* Other oxidizing agents may also be used, such as potassium permanganate or potassium chromate. Browning and Scott, Amer. Jour. Sci. XLIV, 313; XLVI, 663).

B. Characteristics. The germanium compounds are known in two conditions of oxidation; those of the higher form are the more stable and comprise the larger group. Germanium resembles carbon and silicon in the formation of a chloroform, and tin in the formation of two sulphides which dissolve in ammonium sulphide, giving sulpho salts. The sulphide GeS_2 is a white powder slightly soluble in water, and less soluble in strong hydrochloric acid. It is soluble in ammonia and in the alkali sulphides. The lower sulphide, GeS, when precipitated, is of a reddish-brown color; when obtained by the reduction of the higher sulphide it is a grayish-black crystalline substance of metallic luster. This sulphide, also, is slightly soluble in water. The dioxide is a white powder soluble in alkalies, but almost completely insoluble in acids. The tetrachloride is a liquid which fumes in damp air and is decomposed by water. A very characteristic reaction for this element is the precipitation of gelatinous potassium-germanium fluoride, K_2GeF_6, by the addition of hydrofluoric acid and potassium chloride to solutions containing it (Kruss and Nelson, Ber. Dtsch. chem. Ges. xx, 1696; Buchanan, J. Ind. Eng. Chem. VIII, 585). Germanium compounds give a characteristic spark spectrum in the blue and violet.

Estimation. Germanium is usually precipitated as the sulphide, converted by nitric acid into the oxide (GeO_2), and weighed as such.

Separation. Germanium may be separated from most of the elements by the formation of a soluble sulpho salt with ammonium sulphide; when the solution is acidified the sulphide is precipitated. Germanium may be separated from arsenic, antimony, and tin as follows: the solution of the sulpho salts is exactly neutralized with sulphuric acid, allowed to stand twelve hours, and filtered; the filtrate is evaporated to a small volume, treated with ammonia and sulphate of ammonium, acidified with sulphuric acid, and saturated with hydrogen sulphide. Germanium sulphide is precipitated (Truchot, Les Terres Rares, 294).

CHAPTER VII.

VANADIUM, V, 51.

Discovery. As early as 1801 Del Rio announced the discovery of a new metal in a lead ore from Zimapan, Mexico. He named it Erythronium (*ἐρυθρός, red*), because its salts became red when heated with acids (Annal. der Phys. u. Chem. LXXI, 7). Four years later Collet Descotils examined the supposed metal and pronounced it an impure oxide of chromium,—a conclusion that Del Rio himself came to accept (Ann. de Chim. LIII, 268).

In 1830 Sefström found an unknown metal in an iron ore from Taberg, Sweden. He proposed for it the name Vanadium, from Vanadis, the Scandinavian goddess more commonly known as Freya (Amer. Jour. Sci. [1] XX, 386) Almost immediately Wöhler showed the identity of vanadium with the metal described by Del Rio (Pogg. Annal. XXI, 49).

Occurrence. Vanadium is found quite widely distributed, always in combination, and in very small quantities:

	Contains V_2O_5.
Vanadinite, $(PbCl)Pb_4(VO_4)_3$	8–21%
Descloizite, $(Pb,Zn)_2(OH)VO_4$	20–22%
Eusynchite, *vid.* Descloizite	17–24%
Dechenite, *vid.* Descloizite	45–47%
Cuprodescloizite, $(Pb,Zn,Cu)_2(OH)VO_4$	17–22%
Calciovolborthite, $(Cu,Ca)_2(OH)VO_4$	37–39%
Carnotite,* $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 8H_2O$	19–20%

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* Amer. Jour. Sci. X, 138; XXXIII, 574.

	V_2O_4	Contains V_2O_5.
Brackebuschite, formula doubtful		24–25%
Psittacinite, formula doubtful		17–26%
Volborthite, " "		14–15%
Pucherite, $BiVO_4$		22–27%
Roscoelite, silicate, formula doubtful		21–29%
Ardennite, " " "		traces–9%
Mottramite, $(Cu,Pb)_5V_2O_{10}\cdot 2H_2O$		17–18%
Chileite, *vid.* Mottramite		13–14%
Vanadiolite, silico-calcium vanadate		44–45%
Vanadic ocher		100%
Bismuth ocher, formula doubtful		1–29%
Patronite,* VS_4+nS		18–19% V.
Sulvanite, $3Cu_2S\cdot V_2S_5$		12–14%
Pintadoite, $Ca_2V_2O_7\cdot 9H_2O$		39–40%
Uvanite, $(UO_2)_2V_6O_{17}\cdot 15H_2O$		37–38%
Minasragrite, $V_2O_4\cdot 3SO_3\cdot 16H_2O$	(24–25%)	
Fernandinite, $CaO\cdot V_2O_4\cdot 5V_2O_5\cdot 14H_2O$	(10–11%)	55–56%
Hewettite, $H_2CaV_6O_{17}\cdot 8H_2O$	(1– 2%)	69–70%
Metahewettite, *vid.* Hewettite.		
Pascoite, $Ca_2V_6O_{17}\cdot 11H_2O$		64–65%
Aegirite, complex silicate		3– 4%
Aegirite-Augite, complex silicate		2– 3%

Vanadium has been detected also in some copper, lead, and iron ores, in certain clays and basalts, in soda ash and phosphate of soda, and in some hard coals.

Extraction. Vanadium salts may be extracted from mineral sources by the following methods.

(1) The mineral is fused with potassium nitrate, and the potassium vanadate thus formed is extracted with water. By the addition of a soluble lead or barium salt to the solution the lead or barium vanadate is precipitated. This insoluble vanadate is decomposed by means of sulphuric acid, and the barium or lead sulphate is filtered off. By saturation of the filtrate with ammonium chloride the ammonium vanadate is precipitated.

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* Hillebrand, Jour. Amer. Chem. Soc. xxix, 1019.

(2) Finely ground carnotite is decomposed by nitric acid, and the solution is treated with sodium hydroxide and sodium carbonate; the vanadium is left in soluble form as sodium vanadate. If vanadinite is used instead of carnotite the lead must be precipitated from the nitric acid solution by hydrogen sulphide, and the excess of hydrogen sulphide removed from the filtrate by boiling, before the treatment with sodium hydroxide.

(3) The mineral, e. g., carnotite, is fused with acid potassium sulphate, the melt extracted with water, and the solution evaporated, when the double sulphates of vanadium and uranium with potassium crystallize out. The vanadium is reduced by zinc, and precipitated by ammonium hydroxide and ammonium carbonate.

(4) A patented process by J. H. Haynes (Mineral Resources U. S., 1906, page 531) for treatment of carnotite is of interest. The powdered mineral, previously roasted, is agitated with boiling sodium carbonate, which extracts vanadium and uranium. From this solution the uranium is precipitated by sodium hydroxide.

The Element. *A. Preparation.* Elementary vanadium may be prepared (1) by the action of "mischmetal" (metals of Ce and Y groups) on the oxide (V_2O_5) (Muthmann and Weiss, Liebig Ann., CCCXXXVII, 370; CCCLV, 58); (2) by the action of aluminum or carbon on the trioxide (Ruff and Martin, Zeitsch. angew. Chem. XXV, 49).

B. Properties. Vanadium is a non-magnetic, light-gray powder, somewhat crystalline in appearance. It oxidizes slowly in the air at ordinary temperatures, but more rapidly when heated, going through various degrees of oxidation and showing a characteristic color for each oxide,—brown (V_2O), gray (V_2O_2), black (V_2O_3), blue (V_2O_4), and red (V_2O_5). Upon the application of heat vanadium unites with chlorine, forming the chloride VCl_4; at a red heat it combines with nitrogen, giving the nitride VN. It is insoluble in hydrochloric and dilute sulphuric acids, and soluble in nitric, hydrofluoric, and concentrated sulphuric acids. It is not attacked by alkaline solutions, but with melted alkalies forms the alkali vanadates, with the evolution of hydrogen. The specific gravity of vanadium is 5.68. The melting-point of the metal is 1720° C. It forms alloys with iron and aluminum.

Compounds.* *A. Typical forms.* The following may be considered typical compounds of vanadium:

Oxides	V_2O	V_2O_2	V_2O_3†	V_2O_4	V_2O_5
Chlorides		VCl_2	VCl_3	VCl_4	
Oxychlorides			$VOCl$	$VOCl_2$	
Bromide			VBr_3		
Oxybromides				$VOBr_2$	$VOBr_3$
Fluorides			$VF_3 + 6H_2O$		VF_5
Double fluorides			VF_3 with KF, CoF_2, NiF_2, etc.		
Sulphides		V_2S_2	V_2S_3		$V_2S_3O_2$ V_2S_5
Sulpho salts					Na_3VS_3O $(NH_4)_3VS_4$, etc.
Sulphate		VSO_4	$V_2(SO_4)K_2SO_4 + 24H_2O$		$V_2O_2(SO_4)_2$
Nitrides			VN		VN_2
Vanadates, ortho,					$\overset{\mathrm{I}}{R}_3VO_4$
pyro,					$\overset{\mathrm{I}}{R}_4V_2O_7$
meta,					$\overset{\mathrm{I}}{R}VO_3$
complex,	V_2O_5 with P_2O_5, MoO_3, WO_3, SiO_2, AsO_5, etc.				

B. Characteristics. The vanadium compounds are known in five conditions of oxidation, represented by the five oxides. Of these conditions the highest is the most stable and is known in the largest number of salts, the vanadates. Vanadic pentoxide is reddish yellow in color, and, like phosphoric pentoxide, it dissolves readily in the alkali hydroxides and carbonates. The alkali vanadates thus formed are of the ortho, pyro, and meta types, ($\overset{\text{I}}{R}_3VO_4$; $\overset{\text{I}}{R}V_2O_7$; $\overset{\text{I}}{R}VO_3$). The vanadates are generally pale yellow in color. They are soluble in the stronger acids and with the exception of the alkali vanadates insoluble in water. Vanadic acid is easily reduced by reducing agents to the tetroxide condition, when the solution becomes blue. More powerful reducing agents carry the reduction further, to the trioxide, or even the dioxide condition, but only long-continued heating in a current of hydrogen brings about the reduction to the monoxide and the element.

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* See also Das Vanadin und seine Verbindungen, Ephraim, pub. by Ferdinand Enke, Stuttgart, 1904; Rütter, Zeitsch. anorg. Chem. LII, 368; Prandtl, Ber. Dtsch. chem. Ges. XL, 2125; XLVIII, 692; Ztschr. anorg. chem. LXXXII, 103; Koppel, Zeitsch. Electrochem. X, 141; Wedekind, Ber. Dtsch. chem. Ges. XLVI, 1885, 1198; Barbieri, Atti accad. Lincei XXIV, I, 435; Ruff, Ber. Dtsch. chem. Ges. XLIV, 506, 2534.

† Dutton (Jour. Amer. Med. Asso., June 3, 1911) describes a new form of poisoning called Vanadiumism, caused by exposure to the fumes of vanadium trioxide.

Hydrogen sulphide, acting upon vanadic acid, reduces it to the tetroxide condition or even below, with a separation of sulphur. Ammonium sulphide gives the dark-brown solution of a sulpho salt, ($(NH_4)_3S_3VO$?), and this solution, when acidified, gives a brown oxysulphide ($V_2S_3O_2$). Vanadium resembles arsenic, phosphorus, and nitrogen, both in the chemical structure of its compounds and in their behavior toward reagents.

Estimation.* *A. Gravimetric.* Vanadium is usually weighed as the pentoxide, (V_2O_5), obtained (1) by precipitation of lead or barium vanadate, treatment with sulphuric acid, filtration, evaporation of the filtrate, and ignition; (2) by precipitation of mercury vanadate and ignition, the pentoxide being left; (3) by precipitation of the ammonium salt by ammonium chloride and ignition (Berzelius, Pogg. Annal. XXII, 54; Gibbs, Amer. Chem. Jour. V, 371;

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* See Die analytische Chemie des Vanadins, V. von Klecki, pub. by Leopold Voss, Hamburg, 1894; Campagne, Ber. Dtsch. chem. Ges. XXXVI, 3164; Beard, Ann. Chim. anal. et appl. X, 41; Chem. Zentr. 1905 [I], 960. For estimation in ores, see also Low's Technical Methods of Ore Analysis; Blair, Jour. Amer. Chem. Soc. XXX, 1229; Campbell, *ibid.* XXX, 1233.

Gooch and Gilbert, Amer. Jour. Sci. [4] XIV, 205); or (4) by precipitation with "cupferron" (Turner, *ibid.* XLI, 339).

B. Volumetric. Vanadium may be estimated volumetrically (1) by reduction from the condition of the pentoxide to that of the tetroxide by sulphur dioxide, hydrogen sulphide, or zinc and free acid, and reoxidation by permanganate (Hillebrand, Jour. Amer. Chem. Soc. XX, 461; Gooch and Gilbert, Amer. Jour. Sci. [4] XV, 389); (2) by effecting the reduction by boiling with hydrochloric acid or with potassium bromide or iodide in acid solution, according to the typical equation $V_2O_5 + 2HCl = V_2O_4 + H_2O + Cl_2$. The chlorine, bromine, or iodine may be distilled and determined by suitable means in the distillate (Holverscheit, Dissertation, Berlin, 1890; Friedheim, Ber. Dtsch. chem. Ges. XXVIII, 2067; Gibbs, Proc. Amer. Acad. X, 250; Gooch and Stookey, Amer. Jour. Sci. [4] XIV, 369; Gooch and Curtis, Amer. Jour. Sci. [4] XVII, 4), or the residue after boiling may be rendered alkaline by potassium bicarbonate, and reoxidation effected by standard iodine solution (Browning, Amer. Jour. Sci. [4] II, 185); (3) the reduction may be accomplished by boiling with tartaric, oxalic, or citric acid, and reoxidation effected as outlined above (Browning, Zeitsch. anorg. Chem. VII, 158, and Amer. Jour. Sci. [4] II, 355); (4) or sodium thiosulphate may be the reducing agent (Oberhelman, Amer. Jour. Sci. XXXIX, 530). (5) Vanadium and molybdenum may be estimated when together by heating their acids in the presence of sulphuric acid and treating with sulphur dioxide, which reduces the vanadium to the condition of the tetroxide, without affecting the molybdic acid. The vanadium may be estimated as in (1) by permanganate. The oxidized solution may then be passed through a Jones reductor into a receiver charged with a ferric salt. This process reduces the molybdenum to the sesquioxide (Mo_2O_3) condition and the vanadium to the dioxide (V_2O_2) condition, and registers the reduction in the ferric salt. The reoxidation is again effected with permanganate and the amount of vanadium being known from the first titration the molybdenum may be calculated from the second (Edgar, Amer. Jour. Sci. XXV, (1908), 332). (6) By a similar process of differential reduction and oxidation Edgar (Amer. Jour. Sci. XXVI, (1908), 79), estimates iron and vanadium in the presence of each other. After the solution containing vanadic acid and iron has been reduced by sulphur dioxide the oxidation by permanganate proceeds according to the equation:

$$5V_2O_4+10FeO+4KMnO_4=5V_2O_5+5Fe_2O_3+2K_2O+4MnO.$$

After the reduction by zinc in the Jones reductor the oxidation is as follows:

$$5V_2O_2+10FeO+8KMnO_4=5V_2O_5+5Fe_2O_3+4K_2O+8MnO.$$

From these equations, the amount of permanganate used being known, the amount of iron and vanadium present may be calculated.

Separation. Vanadium may be separated from the majority of the metallic bases (1) by fusion of material containing it with sodium carbonate and potassium nitrate and extraction with water, vanadium dissolving as sodium vanadate; or (2) by treatment of a solution containing a vanadate with ammonium sulphide in excess, vanadium remaining in solution as a sulpho salt.

From arsenic vanadium may be separated (1) by treatment with hydrogen sulphide, after reduction by means of sulphur dioxide, the arsenic being precipitated as the sulphide As_2S_3; (2) by heating the sulphides of vanadium and arsenic in a current of hydrochloric-acid gas at 150° C., the arsenic forming a volatile compound (Field and Smith, Jour. Amer. Chem. Soc. XVIII, 1051).

From phosphorus vanadium may be separated by reduction of vanadic acid by means of sulphur dioxide, and precipitation of the phosphorus as phosphomolybdate.

From molybdenum the separation may be accomplished by the action of hydrogen sulphide upon a solution of vanadic and molybdic acids under pressure,—molybdenum sulphide being precipitated,—or by the action of ammonium chloride in excess upon a solution containing an alkali vanadate and molybdate,—ammonium metavanadate being precipitated (Gibbs, Amer. Chem. Jour. v, 371).

From tungsten vanadium may be separated by the ammonium chloride method (*vid.* Separation from molybdenum, above) (Gibbs, Amer. Chem. Jour. v, 379).

From uranium vanadium may be separated (1) by sodium hydroxide, as in Experiment 1; (2) by treatment with chlorine (Barker and Schmidt, Met. Chem. Eng. xiv, 18).

EXPERIMENTAL WORK ON VANADIUM.

Experiment 1. *Extraction of vanadium from carnotite.* Treat 20 grm. of the finely powdered mineral with hydrochloric acid, heat until nothing further dissolves, dilute, pass hydrogen sulphide, and filter. Evaporate the filtrate nearly to dryness, add enough nitric acid to oxidize the vanadium to vanadic acid. To the oxidized solution add sodium hydroxide in excess, warm, and filter. The filtrate should contain sodium vanadate together with an excess of sodium hydroxide. Neutralize carefully with acetic acid and test for vanadium by any of the following experiments:

Experiment 2. *Formation of insoluble vanadates of lead, silver, barium and ammonium,* ($\overset{II}{R}_3(VO_4)_2$, *ortho; or* $\overset{II}{R}(VO_3)_2$, *meta*).

To separate portions of a solution of an alkali vanadate (ortho or meta) add (*a*) a solution of lead acetate; (*b*) silver nitrate; (*c*) barium chloride; (*d*) ammonium chloride (in solid form). Try the action of nitric and acetic acids upon the precipitated salts.

Experiment 3. *Formation of vanadium pentoxide,* (V_2O_5), *from ammonium vanadate.* Evaporate a solution of ammonium vanadate to dryness and ignite. Note the crystals of the pentoxide.

Experiment 4. *Precipitation of vanadium oxysulphide,* ($V_2S_3O_2$). (*a*) To a solution of an alkali vanadate add ammonium sulphide. Note the darkening in color ($(NH_4)_3S_3VO$?). Acidify the solution with hydrochloric acid. Note the precipitation of the oxysulphide.

(*b*) Note that hydrogen sulphide in an acid solution precipitates sulphur and leaves a blue solution (V_2O_4).

(*c*) Pass hydrogen sulphide into a solution of a vanadate made strongly alkaline with ammonium hydroxide. Note the red color.

Experiment 5. *Reduction of vanadic acid,* (V_2O_5). (*a*) To a solution of an alkali vanadate add a crystal of tartaric acid and boil. Note the yellow-red color of the vanadic acid when the tartaric acid is first added, and the change to blue (V_2O_4) produced on boiling.

(*b*) Neutralize the blue solution obtained in (*a*) with sodium or potassium bicarbonate, and add a solution of iodine in potassium iodide until, after the liquid has stood for a few moments, the color of the iodine remains. Bleach the excess of iodine with an alkaline solution of arsenious oxide. Note that the blue color has disappeared and the vanadium is in the condition of the pentoxide (V_2O_5).

(*c*) Try the action of other reducing agents upon vanadic acid, e.g. oxalic acid, hydrochloric acid, stannous chloride, zinc and hydrochloric acid, etc. Note that the zinc and hydrochloric acid carry the reduction below the tetroxide condition (V_2O_4) *

Experiment 6. *Delicate tests for vanadium. Formation of pervanadic acid,* (HVO_4). (*a*) Acidify a solution of an alkali vanadate and add hydrogen dioxide. Note the red color (Maillard).

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* The following series of colors obtained by the action of a reducing agent upon vanadic acid is given by Roscoe: yellow (V_2O_5), green ($V_2O_5+V_2O_4$), bluish-green ($V_2O_5+V_2O_4$), blue (V_2O_4), greenish-blue ($V_2O_4+V_2O_3$), green ($V_2O_3+V_2O_2$), bluish-violet ($V_2O_3+V_2O_2$), lavender or violet (V_2O_2).

(*b*) Bring a few drops of the vanadium solution into contact with a drop of strong sulphuric acid to which a crystal of strychnine sulphate has been added. Note the color, changing from violet to rose.

Experiment 7. Borax-bead tests for vanadium. Fuse a little ammonium vanadate into a borax bead and test the action of the reducing and oxidizing flames upon it.

NIOBIUM (COLUMBIUM), Nb(Cb), 93.5; TANTALUM, Ta, 181.5.

Discovery. Hatchett, while working with some chromium minerals in the British Museum in 1801, came across a black mineral very similar to those upon which he was engaged (Phil. Trans. Roy. Soc. (1802), 49). He obtained permission to examine it and found it to consist almost wholly of iron and an earth which did not conform to any known test. He described it as "a white, tasteless earth, insoluble in hot and cold water, acid to litmus, infusible before the blowpipe, and not dissolved by borax." The only acid which dissolved it was sulphuric. Since the mineral was of American origin, coming from Connecticut, the discoverer named it Columbite, and the element Columbium.

About a year later Ekeberg (Crell Annal. (1803) 1, 3), while investigating a mineral from Kimito, Finland, which closely resembled columbite, discovered a "metal" which resembled tin, tungsten, and titanium. It proved to be none of these, but in fact a new element. He named it Tantalum, "because even when in the midst of acid it was unable to take the liquid to itself." Indeed, insolubility in acid seemed to be the chief characteristic of the new substance.

The apparent similarity of columbium and tantalum suggested that they might be identical, and in order to settle this question Wollaston (Phil. Trans. Roy. Soc. XCIX, 246) in 1809 began to work on tantalite and a specimen of the same columbite that Hatchett had examined. He found that the freshly precipitated acids were both soluble in concentrated mineral acids; if they were dried it was necessary to fuse them both with caustic alkalies before they could be dissolved. Both were held up if ammonium hydroxide was added in the presence of citric, tartaric, or oxalic acid. Having found practically the same reactions with both acids, he concluded that the elementary substances were the same. The specific gravity of tantalite, however, was 7.95, and that of columbite 5.91. This he explained by suggesting different conditions of oxidation or different states of molecular structure. These conclusions were accepted, and for many years the element was called indifferently tantalum and columbium.

In 1844 Rose began to investigate the same subject. His work on the columbites of Bodenmais and Finland led him to the belief that there were two distinct acids in the columbite from Bodenmais, one similar to that in tantalite, the other containing a new element, to which he gave the name Niobium, from Niobe, daughter of Tantalus. Though niobium proved to be Hatchett's columbium, Rose's name for the element has been the one more generally adopted. The name columbium is now, however, growing in favor, especially among American chemists.

Occurrence.* Niobium and tantalum are found, each in combination, in various rare minerals. They usually, though not invariably, occur together.

	Contains	
	Nb_2O_5	Ta_2O_5
Pyrochlore, $RNb_2O_6 \cdot R(Ti,Th)O_3$	47–58%	
Chalcolamprite, *vid.* Pyrochlore	59–60%	
Marignacite, *vid.* Pyrochlore	55–56%	5– 6%
Koppite, $R_2Nb_2O_7 \cdot \frac{2}{5}NaF$	61–62%	

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* See also Schilling, Zeitsch. angew. Chem. (1905), 883.

	Contains	
	Nb_2O_5	Ta_2O_5
Hatchettolite, $2R(Nb,Ta)_2O_6 \cdot R_2(Nb,Ta)_2O_7$	63–67%*	
Microlite, $Ca_2Ta_2O_7$	7– 8%	68–69%
Fergusonite, $(Y,Er,Ce)(Nb,Ta)O_4$	14–46%	4–43%
Samirésite, complex	45–46%	3– 4%
Blomstrandine-Priorite, complex	18–37%	0–1%
Sipylite, $\overset{III}{R}NbO_4$	47–48%	1– 2%
Columbite, $(Fe,Mn)(Nb,Ta)_2O_6$	26–77%	1–77%
Tantalite, $FeTa_2O_6$	3–40%	42–84%
Neotantalite, *vid.* Tantalite	23%	60–61%
Skogbölite, $FeTa_2O_6$	3–40%	42–84%
Tapiolite, $Fe(Nb,Ta)_2O_6$	11–12%	73–74%
Mossite, $Fe(Nb,Ta)_2O_6$	83%*	
Yttrotantalite, $\overset{II}{R}\overset{III}{R}_2(Ta,Nb)_4O_{15}$	12–13%	46–47%
Samarskite, $\overset{III}{R}_2\overset{II}{R}_3(Nb,Ta)_6O_{21}$	41–56%	14–27%
Nohlite, *vid.* Samarskite	50–51%	
Loranskite, complex		47%
Risörite, yttrium niobate	36–37%	4%
Stibiotantalite, $Sb_2O_3(Ta,Nb)_2O_5$?	7·5 %	51%
Ånnerödite, complex	48–49%	
Hielmite, complex	4–16%	55–72%
Æschynite, $\overset{III}{R}_2Nb_4O_{13} \cdot \overset{III}{R}_2(Ti,Th)_5O_{13}$	32–33%	21–22%
Polymignite, $5RTiO_3 \cdot 5RZrO_3 \cdot R(Nb,Ta)_2O_6$	11–12%	1– 2%
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$	18–35%	
Polycrase, $\overset{III}{R}(NbO_3)_3 \cdot 2\overset{III}{R}_2(TiO_3)_3 \cdot 3H_2O$	19–25%	0– 4%
Wöhlerite, $12R(Si,Zr)O_3 \cdot RNb_2O_6$	12–14%	
Låvenite, $R(Si,Zr)O_3 \cdot Zr(SiO_3)_2 \cdot RTa_2O_6$	0– 5%*	
Dysanalyte, $6RTiO_3 \cdot RNb_2O_6$	0–23%	0– 5%
Kochelite, *vid.* Fergusonite	29–30%	
Arrhenite, complex	2– 3%	21–22%

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* $Nb_2O_5+Ta_2O_5$.

	Contains	
	Nb_2O_5	Ta_2O_5
Blomstrandite, complex	49–50%*	
Rogersite,	18–20%	
Adelpholite, *vid.* Sipylite	41–42%*	
Vietingshofite, *vid.* Samarskite	51%*	
Eucolite, complex silicates	2– 4%*	
Melanocerite, complex silicates		3– 4%
Caryocerite, *vid.* Melanocerite		3.1%
Steenstrupine, *vid.* Melanocerite	0–1.5%*	
Cyrtolite, silicate	0–1.5%*	
Naegite, silicate	4%	7%
Tritomite, complex silicates		1– 3%
Cassiterite (Ainalite), SnO_2		0– 9%

Extraction. Salts of niobium and tantalum may be extracted from columbite or tantalite by either of the following methods:

(1) The mineral is fused with six parts of potassium bisulphate, the fused mass is pulverized and treated with hot water and dilute hydrochloric acid. The residue is then digested with ammonium sulphide to remove tin, tungsten, etc., and again warmed with dilute hydrochloric acid. After this treatment it is washed thoroughly with water and dissolved in hydrofluoric acid. Filtration is followed by the addition of potassium carbonate to the clear solution until a precipitate begins to form. The potassium and tantalum double fluoride separates first in needle-like crystals, after which the niobium oxyfluoride crystallizes in plates.

(2) The mineral is fused with three parts of acid potassium fluoride (*vid.* Experiment 1).

The Elements. I. NIOBIUM. *A. Preparation.* The element niobium may be obtained (1) by reducing the oxide with aluminum (Goldschmidt reaction); (2) by mixing the pentoxide with paraffin, drawing into fibers, and reducing to the tetroxide by heating with carbon. The tetroxide, being a conductor, is reduced to the metal by heating highly *in vacuo* (von Bolton, Zeitsch. Electrochem. XIII, 145); (3) by heating the oxide with "mischmetal" (Muthmann and Weiss, Liebig Ann. CCCXXXVII, 370; CCCLV, 58).

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* $Nb_2O_5+Ta_2O_5$.

B. Properties. Niobium is a metallic element of steel-gray color and brilliant luster. Heated in the air it is only slowly oxidized to Nb_2O_4. It is practically unattacked by acids, except by a mixture of nitric and hydrofluoric acids, but is attacked by fused alkalies and at red heat by chlorine. It combines with hydrogen and nitrogen. It is as hard as wrought iron, and is malleable and ductile. Its fusing-point is 1950° C.,* and its specific gravity is about 7.

II. TANTALUM.† *A. Preparation.* Elementary tantalum may be obtained (1) by heating the potassium and tantalum fluoride (K_2TaF_7) with potassium and extracting the potassium fluoride with water; (2) by heating the oxide with "mischmetal."

B. Properties. Tantalum in the elementary condition is a little darker in color than platinum, and is about as hard as soft steel. It can be hammered into plates and drawn into wire. In the cold it is very inert. Heated to 400° C. it becomes yellow, and to 600° bluish. At low redness it burns to the oxide. Its melting-point is given as 2850° C. (von Pirani) and 2900° C. (Waidner).‡ It combines at low redness with hydrogen,§ nitrogen, and chlorine. It combines readily with carbon, forming several carbides. The metal is not attacked by hydrochloric, nitric, or sulphuric acid, but is attacked by hydrofluoric acid and by fused alkalies. The specific gravity of melted and drawn tantalum is 16.8; that of the metal in powder form (hydrogen and oxygen being present), 14.

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* U. S. Bureau of Standards gives 1700° C. ?

† Von Bolton, Zeitsch. angew. Chem. (1906), 1537; Muthmann, Liebig Ann. CCCLV, 58.

‡ Waidner and Burgess, J. physique VI, 380; Chem. Abs., Amer. Chem. Soc. II, 739 (Mar. '08); von Pirani and Meyer, Zeitsch. f. Electrochem. XVII, 908.

§ Sieverts and Bergner, Ber. Dtsch. chem. Ges. XLIV, 2394.

Compounds.* *A. Typical forms.* The following are typical compounds of niobium and tantalum:

Oxides..........	Nb_2O_2	
	Nb_2O_4	Ta_2O_4
	Nb_2O_5	Ta_2O_5
Chlorides.......	$(Nb_6Cl_{12})Cl_2 \cdot 7H_2O$†	$(Ta_6Cl_{12})Cl_2 \cdot 7H_2O$†
	$NbCl_3$	
	$NbCl_5$	$TaCl_5$
Oxychloride.....	$NbOCl_3$	
Bromides.......	$NbBr_5$	$TaBr_5$
Oxybromide.....	$NbOBr_3$	
Fluorides.......	NbF_5	TaF_5
Oxyfluoride.....	$NbOF_3$	
Fluotantalates ..		K_2TaF_7
		Na_2TaF_7
		$(NH_4)_2TaF_7$
Double fluorides.	$\left.\begin{matrix} xKF \cdot yNbOF_3 \\ xKF \cdot yNbO_2F \end{matrix}\right\}$ (typical)	
Sulphide........	Nb_2OS_3	Ta_2S_4
Silicide.........		$TaSi_2$
Nitride.........		Ta_3N_5
Niobates........	$K_8Nb_6O_{19} + 16H_2O$	
	$K_6Nb_4O_{13} + 13H_2O$	
	$2K_2Nb_4O_{11} + 11H_2O$	
	$K_4Nb_2O_7 + 11H_2O$	
	$Na_{16}Nb_{14}O_{43}$	
	$Na_2Nb_2O_6$, etc.	
Tantalates ‡		Of types $\overset{I}{R}_8Ta_6O_{19}$ and $RTaO_3$, with Na, K, NH_4, Ba, and Mg.

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* See also E. F. Smith and others, Jour. Amer. Chem. Soc. XXVII, 1140, 1216, 1369; XXX, 1637; XXXII, 323, 729; Chabrié, Compt. rend. CXLIV, 804; Ruff and Schiller, Zeitsch. anorg. Chem. LXII, 329.

† For corresponding bromides and iodides, *vid.* (for niobium) Harned, Jour. Amer. Chem. Soc. XXXV, 1078; (for tantalum) Chapin, *ibid.* XXXII, 323.

‡ *Vid.* also Wedekind and Maass, Zeitsch. angew. Chem. XXXIII, 2314.

B. Characteristics. The compounds of niobium closely resemble those of tantalum, both in chemical form and in behavior toward reagents. The two elements are closely associated in minerals (*vid.* Occurrence). The lower oxides of niobium are dark powders which oxidize when heated. The dioxide is soluble in hydrochloric acid, while the tetroxide is not attacked by acids. The pentoxide is a yellowish-white amorphous powder somewhat soluble in concentrated sulphuric acid before ignition, but insoluble after. Niobium pentachloride is a yellow crystalline substance prepared by passing sulphur chloride (S_2Cl_2) in the form of vapor over the pentoxide. It tends to form the oxychloride in the presence of water. It is reduced to the trichloride when its vapor is passed through a red-hot tube. The fluoride is formed by the action of hydrofluoric acid upon the pentoxide

Tantalum tetroxide is a very hard, dark-gray, porous mass which is not attacked by acids. When heated it goes over to the higher oxide. The pentoxide of tantalum is a white powder which is somewhat soluble in acids. The chloride and fluoride of tantalum are formed similarly to the corresponding salts of niobium and resemble them in general behavior. Niobates and tantalates are obtained by fusing the oxides with caustic alkalies; these salts are soluble. The tantalum compounds give no color test with morphia, tannic acid, or pyrogallic acid.

Estimation. *A. Gravimetric.* Niobium and tantalum are ordinarily weighed as the oxides Nb_2O_5 and Ta_2O_5, obtained from ignition of the acids.

B. Volumetric. Niobium may be estimated volumetrically by reduction from the condition of the pentoxide to that of the trioxide by means of zinc and hydrochloric acid in a current of carbon dioxide, and oxidation with permanganate (Osborn, Amer. Jour. Sci. [3] XXX, 329; Levy, Analyst. XL, 204. *Vid.* also Meimberg, Ztschr. angew. Chem. XXVI, 83).

Separation. The method usually employed for the separation of niobium and tantalum from the elements with which they are generally associated—namely, titanium, zirconium, and thorium—is that of fusion with acid potassium sulphate (*vid.* Titanium). From tin and tungsten they may be separated by repeated fusions of the oxides with sodium carbonate and sulphur (E. F. Smith, Proc. Amer. Philos. Soc. XLIV, 157).

The separation of niobium from tantalum is one of the most difficult of analytical problems. Marignac's method* (Ann. Chim. Phys. [4] VIII, 1) is based upon the difference in solubility† between the tantalum-potassium fluoride (K_2TaF_7) and the niobium-potassium oxyfluoride ($2KF \cdot NbOF_3 + H_2O$). Foote and Langley (Amer. Jour. Sci. [4] XXX, 393) have devised an indirect method depending upon the difference in density (Ta_2O_5, 8.716 and Nb_2O_5, 4.552) of the oxides. They use as standards for comparison densities of mixtures of known content.

EXPERIMENTAL WORK ON NIOBIUM AND TANTALUM.

Experiment 1. *Extraction of niobium and tantalum salts from columbite or tantalite.* Mix 5 grm. of the finely ground mineral with 15 grm. of acid potassium fluoride and fuse thoroughly. Pulverize the fused mass and extract with boiling water containing a little hydrofluoric acid. Evaporate to about 200 cm.^{3} and allow the liquid to stand. The potassium and tantalum fluoride separates first in needle-like form; the niobium and potassium oxyfluoride crystallizes in plates on concentration of the solution. The salts of the two elements should be purified as far as possible by fractional crystallizations.

Experiment 2. *Preparation of niobic and tantalic oxides (acids)*, (Nb_2O_5; Ta_2O_5). (*a*) Evaporate to dryness in a lead or platinum dish a solution of potassium and niobium oxyfluoride, add strong sulphuric acid, and heat until all the hydrofluoric acid is expelled and a solution is obtained. Cool the solution, dilute with water, and boil. Niobic acid, (Nb_2O_5), is precipitated. Filter, and test the filtrate with ammonium hydroxide.

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* *Vid.* Meimberg and Winzer, Ztschr. angew. Chem. XXVI, 157; Moir, Chem. Abs. X, 1825.

† K_2TaF_7 is soluble in 151-157 parts of cold water. $2KF \cdot NbOF_3 + H_2O$ is soluble in 12–13 parts of cold water.

(*b*) Repeat the experiment, using a solution of potassium and tantalum fluoride instead of the niobium salt.

(*c*) Test the action of alkali hydroxides or carbonates in excess upon solutions of niobium and tantalum obtained in (*a*) and (*b*).

(*d*) Try the action of the common acids upon freshly precipitated niobic and tantalic acids. Note that hydrogen dioxide aids the solvent action.

Experiment 3. *Effect of fusion with sodium or potassium hydroxide upon niobic and tantalic acids.* (*a*) Melt a gram of sodium or potassium hydroxide in a hard glass tube, add a small quantity of dry niobic acid, and heat again. Note that the fused mass is soluble in water.

(*b*) Repeat the experiment, using dry tantalic acid instead of niobic.

(*c*) Acidify with the common acids portions of the solutions obtained in (*a*) and (*b*).

(*d*) Try the effect of carbon dioxide upon these solutions.

Experiment 4. *Tests for niobium.* (*a*) To separate portions of dry niobic oxide (or acid) add a few drops of strong sulphuric acid, and treat with tannic acid, pyrogallic acid, and morphia, respectively. Note the brown color.

(*b*) Repeat the experiment, using tantalic oxide instead of niobic. Note the absence of color.

(*c*) Try the action of metallic zinc upon an acid solution containing niobium. Note the color. Filter, and add a solution of mercuric chloride. Note the precipitate.

Experiment 5. *Negative tests of niobium and tantalum.* Note that hydrogen sulphide gives no precipitate, and that hydrogen peroxide gives no yellow color with acid solutions containing niobium or tantalum.

CHAPTER VIII.

MOLYBDENUM, Mo, 96.

Discovery. The name Molybdena, derived from *μόλυβδος*, *lead*, was originally applied to a variety of substances containing lead. Later the term was used to designate only graphite and a mineral sulphide of molybdenum which is very similar in appearance to graphite, and which was confused with it. In 1778 Scheele, in his treatise on molybdena (Kong. Vet. Acad. Handl. (1778), 247), showed that it differs from plumbago, or graphite, in that on being heated with nitric acid it yields a peculiar white earth, which he proved to be an acid-forming oxide. This he called "acidum molybdenæ," and he supposed the mineral to be a compound of this oxide with sulphur. In 1790 Hjelm (ibid. (1790), 50; Ann. de Chim. IV, 17) isolated the element.

Occurrence. Molybdenum occurs in combination in minerals which are somewhat widely diffused, though found in small amounts:

	Contains MoO_3
Molybdic ocher or Molybdite, $Fe_2O_3 \cdot 3MoO_3 \cdot 7\frac{1}{2}H_2O$	57–59%
Powellite, $Ca(Mo,W)O_4$	58–59%
Wulfenite, $PbMoO_4$	37–40%
Belonesite, $MgMoO_4$?	78–79%
Pateraite, $CoMoO_4$?	30%
Scheelite, $CaWO_4$	traces–8%
Koechlinite, $Bi_2O_3 \cdot MoO_3$	23–24%
Molybdenite, MoS_2	60% Mo
Ilsemannite, $MoO_2 \cdot 4MoO_3$	68% Mo

Extraction. Molybdenum salts are usually obtained from molybdenite, the most abundant ore, though sometimes from other minerals. The following processes will illustrate the methods employed.

(1) *From molybdenite.* The mineral is roasted until sulphur dioxide is no longer given off and the residue is yellow when hot and white when cold. This residue is dissolved in dilute ammonium hydroxide, and the solution is evaporated to crystallization. Heat drives off the ammonia from the crystals and leaves the trioxide of molybdenum.

(2) *From molybdenite.* The mineral is treated with nitric acid (*vid.* Experiment 1).

(3) *From wulfenite.* The mineral is fused with potassium polysulphide. Upon extraction with water the lead remains insoluble, as the sulphide, and the molybdenum goes into solution as the sulpho salt. The filtrate is acidified with sulphuric acid, and the sulphide of molybdenum is precipitated (Wittstein).

The Element. *A. Preparation.* Elementary molybdenum may be prepared (1) by passing dry hydrogen over either the trioxide or the ammonium salt at red heat; (2) by reducing the chlorides with hydrogen; (3) by heating the oxide (MoO_3) with "misch-metal"; (4) by heating the oxide (MoO_2) with aluminum (Goldschmidt process).

B. Properties. Molybdenum is a gray metallic powder, which is unchanged in the air at ordinary temperatures, but which, when heated, passes gradually into the trioxide. It is insoluble* in hydrochloric, hydrofluoric, and dilute sulphuric acids, but soluble in nitric and concentrated sulphuric acids, in aqua regia, in chlorine water, in melted potassium hydroxide, and in melted potassium nitrate. Its specific gravity is 8.6. Its melting-point is 2550° C.

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* For solubilities *vid.* Ruder, Jour. Amer. Chem. Soc. XXXIV, 387.

Compounds.* *A. Typical forms.* The following are typical compounds of molybdenum:

Oxides......	MoO	Mo_2O_3	MoO_2	Mo_5O_{12}	Mo_3O_8		MoO_3
Chlorides†..	$MoCl_2$	$MoCl_3$	$MoCl_4$			$MoCl_5$	
Oxychlorides.							$MoOCl_4$ MoO_2Cl_2
Bromides....	$MoBr_2$	$MoBr_3$	$MoBr_4$				
Oxybromide..							MoO_2Br_2
Oxyiodide....						MoO_2I	
Fluoride.....							MoF_6
Oxyfluorides.						$MoOF_3\cdot 2KF + H_2O$	$MoO_2F_2\cdot KF + H_2O$
Carbides.....	Mo_2C		MoC				
Silicide......			$MoSi$				
Sulphides....			MoS_2				MoS_3; MoS_4
Sulpho salt...							$\overset{I}{R}_2MoS_4$

Molybdates, many salts of the type $\overset{I}{R}_2MoO_4$, as K_2MoO_4; $CaMoO_4$; $ZnMoO_4$; Ag_2MoO_4; etc. The formula for ammonium molybdate is given as $(NH_4)_6Mo_7O_{24}+4H_2O$. Barbieri has formed a series of molybdates of the rare earths of the type $(NH_4)_3\overset{III}{R}Mo_7O_{24}+12H_2O$, where $\overset{III}{R}$ = Ce, La, Nd, Pr, or Sm.

Molybdenum trioxide combines with phosphoric pentoxide in the following proportions: $P_2O_5:MoO_3::1:24$, $1:22$, $1:20$, $1:18$, $1:16$, $1:15$, $1:5$, as $2K_2HPO_4\cdot 24MoO_3+3H_2O$; $2(NH_4)_3PO_4\cdot 16MoO_3+14H_2O$; etc. It combines with arsenic pentoxide as follows: $As_2O_5:MoO_3::1:20$, $1:18$, $1:16$, $1:6$, $1:2$, as $As_2O_5\cdot 20MoO_3+27H_2O$; $10NH_3\cdot As_2O_5\cdot 16MoO_3+14H_2O$; etc.

B. Characteristics. The molybdenum compounds are known in various conditions of oxidation (*vid.* Typical Forms), of which the highest, (MoO_3), is the most stable and comprises the largest number of salts. The trioxide is white to pale yellow, and dissolves in potassium, sodium, and ammonium hydroxides, forming the molybdates. The alkali molybdates are the only soluble molybdates. When strong reducing agents, such as zinc and hydrochloric acid, act upon acid solutions of molybdates, the reduction is said to go as far as the oxide Mo_5O_7, the solution passing through the colors of the various oxides, violet, blue, and black. The oxide Mo_5O_7, however, is very sensitive to oxidation, for it is changed in the air to the sesquioxide (Mo_2O_3) as soon as the reducing action has ceased. Acid solutions of the lower oxides give, on treatment with the alkali hydroxides, the corresponding hydroxides of molybdenum, $Mo_2O_3 \cdot 3H_2O$; $MoO_2 \cdot xH_2O$; etc. The sulphide (MoS_3) is obtained by treating a molybdate with ammonium sulphide and acidifying. Its color is reddish brown.

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* See also Bailhache, Compt. rend. cxxxv, 862; Mylius, Ber. Dtsch. chem. Ges. xxxvi, 638; Rosenheim, Zeitsch. anorg. Chem. xxxiv, 427; xlvi, 311; xlix, 148; l, 320; liv, 97; lxxix, 292; lxxxiv, 217; xci, 75; Grossmann, Zeitsch. anorg. Chem. xli, 43; Zeitsch. phys. Chem. lvi, 577; liv, 40; Weinland, Zeitsch. anorg. Chem. xliv, 81; Sand, Ber. Dtsch. chem. Ges. xxxviii, 3384; xl, 4504; Copaux, Ann. chim. phys. [8] vii, 118; Bull. Soc. franç. Minéral. xxx, 292 (Oct. 1907), or Chem. Zentr. (1908) i, 711; Lancien, Bull. d. Sciences Pharmacol. xv, 132, or Chem. Zentr. (1908) i, 1763; Ruff, Ber. Dtsch. chem. Ges. xl, 2926; Hilpert, Ber. Dtsch. chem. Ges. xlvi, 1669.

† Michael and Murphy, Amer. Chem. Jour. xliv, 365.

Estimation.* *A. Gravimetric.* Molybdenum is generally weighed as the oxide (MoO_3), obtained (1) by ignition of ammonium molybdate; (2) by precipitation of mercury molybdate and ignition; or (3) by precipitation of the sulphide and conversion into the oxide by treatment with nitric acid.

B. Volumetric. Soluble molybdates may be reduced in acid solution (1) by boiling with potassium iodide. (*a*) The iodine thus liberated may be passed into potassium iodide and estimated by standard thiosulphate, the amount of molybdenum present being calculated from the equation $2MoO_3 + 2HI = Mo_2O_5 + I_2 + H_2O$; or, (*b*) after the iodine has been removed by boiling, the residual solution may be rendered alkaline by potassium bicarbonate and reoxidized by standard iodine solution or potassium permanganate (Mauro and Danesi, Zeitsch. anal. Chem. XX, 507; Friedheim and Euler, Ber. Dtsch. chem. Ges. XXVIII, 2066; Gooch and Fairbanks, Amer. Jour. Sci. [4] II, 156; Gooch and Pulman, Amer. Jour. Sci. [4] XII, 449); (2) by passing the solution over zinc in a Jones reductor into a flask charged with a ferric salt. The molybdic acid, reduced to the sesquioxide (Mo_2O_3) in the reductor is reoxidized by the ferric salt, and the ferrous salt formed is titrated by permanganate (Randall, Amer. Jour. Sci. XXIV (1907), 313). See also under Vanadium a volumetric process for the estimation of vanadium and molybdenum in the presence of each other, page 112.

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* For the estimation in ores, see Low's Technical Methods of Ore Analysis; Blair, Jour. Amer. Chem. Soc. xxx, 1229.

Separation. The general methods for the separation of molybdenum from the metals* and alkali earths are the same as those described under Vanadium.

From arsenic and phosphorus, when present as arsenic and phosphoric acids, molybdenum may be separated by magnesium chloride mixture in ammoniacal solution, ammonium-magnesium arseniate and phosphate being precipitated (Gibbs, Amer. Chem. Jour. VII, 317; Gooch, Amer. Chem. Jour. I, 412).

For the separation from vanadium, *vid.* Vanadium.

From tungsten molybdenum may be separated (1) by the action of warm sulphuric acid of specific gravity 1.37 upon the oxides (MoO_3 and WO_3), molybdic acid dissolving (Ruegenberg and Smith, Jour. Amer. Chem. Soc. XXII, 772); (2) by heating the oxides with hydrochloric-acid gas at 250°–270° C., the molybdenum compound ($MoO_3 \cdot 2HCl$) being volatilized (Pechard, Compt. rend. CXIV, 173; Debray, *ibid.* XLVI, 1101); (3) by precipitation of tungstic acid by means of stannous chloride (Marbaker, Jour. Amer. Chem. Soc. XXXVII, 86).

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* Molybdenum and tungsten may be separated electrolytically from copper, lead, and mercury (McCay and Furman, Jour. Amer. Chem. Soc. XXXVIII, 640).

EXPERIMENTAL WORK ON MOLYBDENUM.

Experiment 1. *Extraction of molybdenum salts from molybdenite*, (MoS_2). Heat 5 grm. of the finely powdered mineral with nitric acid until the dark color has disappeared. Evaporate to dryness, wash the residue in warm dilute nitric acid, then in water, and dissolve it in ammonium hydroxide. Filter, and evaporate the filtrate to a small volume. Ammonium molybdate crystallizes out, which may be converted into the trioxide by careful ignition.

Experiment 2. *Precipitation of the sulphides of molybdenum*, (MoS_2; MoS_3). (*a*) Through a solution of ammonium molybdate acidified with hydrochloric acid pass hydrogen sulphide. Note the gradual change of color of the solution, from red-brown to blue, and the partial precipitation of the sulphide MoS_2.

(*b*) To a solution of ammonium molybdate add ammonium sulphide, or pass hydrogen sulphide through an alkaline solution of a molybdate. Note the yellow-brown color ($(NH_4)_2MoS_4$, typical). Acidify the solution and note the brown precipitate (MoS_3).

Experiment 3. *Precipitation of ammonium phosphomolybdate* ($3(NH_4)_2O \cdot P_2O_5 \cdot 24(MoO_3) + 2H_2O$). To a solution of ammonium molybdate acidified with nitric acid add a drop of a solution of sodium phosphate, and warm gently. Note the yellow precipitate.

Experiment 4. *Precipitation of the molybdates of silver, lead, and barium*, (Ag_2MoO_4, $PbMoO_4$, and $BaMoO_4$, *typical*). To separate solutions of ammonium molybdate, neutral or faintly acid with acetic acid, add solutions of silver nitrate, lead acetate, and barium chloride respectively. Note the solvent action of nitric acid upon the precipitates.

Experiment 5. *Reduction of molybdic acid*, (MoO_3).

(*a*) Put a piece of metallic zinc into a solution of ammonium molybdate and add hydrochloric acid until the action starts. Note the change in color of the solution as the reduction proceeds (reddish yellow, violet, bluish, black). To a few drops of the solution after reduction add potassium or sodium hydroxide. Note the dark-brown precipitate of the lower hydroxides of molybdenum ($Mo_2(OH)_6$, etc.) mixed with the hydroxide of zinc.

(*b*) Try the reducing action of stannous chloride upon a molybdate in solution. Try also the action of hydrazine sulphate.

(*c*) To a dilute solution of a molybdate which has been treated with zinc and hydrochloric acid, add some potassium sulphocyanide in solution. Note the red color. Try the effect of adding ether and shaking.

(*d*) To a few drops of a solution of a molybdenum compound add a little strong sulphuric acid, and evaporate nearly to dryness in a porcelain dish. Note the blue color.

Experiment 6. *Formation of a permolybdate.* To a solution of a molybdenum compound add ammonium hydroxide and hydrogen dioxide. Note the red color of the ammonium permolybdate.

Experiment 7. *Formation of molybdenum ferrocyanide.* To a solution of a molybdate acidified with hydrochloric acid add a solution of potassium ferrocyanide. Note the brown precipitate and its solubility in ammonium hydroxide.

TUNGSTEN, W. 184.

Discovery. The minerals scheelite, formerly called tungsten (i.e. "heavy stone"), and wolframite have long been known, but until about the middle of the eighteenth century they were regarded as tin ores. In 1781 Scheele (Kong. Vet. Acad. Handl. (1781), 89) demonstrated that scheelite contained a peculiar acid which he named Tungstic acid. Two years later the brothers D'Elhujar showed the presence of the same acid in wolframite.

Occurrence. Tungsten is found combined in minerals which are often associated with tin ores:

	Contains WO_3.
Wolframite, $(Fe,Mn)WO_4$.	74–78%
Scheelite, $CaWO_4$.	71–80%
Hübnerite, $MnWO_4$.	73–77%
Cuprotungstite, $CuWO_4$.	56–57%
Cuproscheelite, $(Ca,Cu)WO_4$	76–80%
Powellite, $Ca(Mo,W)O_4$	10–11%
Stolzite, $PbWO$	51 *circa*
Raspite, $PbWO_4$.	49 "
Reinite, $FeWO_4$.	75–76%
Ferberite, $FeWO_4$.	69–70%
Ferritungstite, $Fe_2O_3 \cdot WO_3 \cdot 6H_2O$.	42–45%
Yttrotantalite, complex niobate-tantalate	2– 4%
Tungstite, WO_3	100 *circa*
Meymacite, hydrated WO_3	71–75%
Tungstenite, WS_2	44–45% W

Extraction.[*] Tungstic acid is usually extracted from wolframite. Any of the processes here indicated may be followed:

(1) 5 parts of the mineral are fused with 8.5 parts of dry sodium carbonate and 1.5 parts of sodium nitrate. On treatment of the fused mass with water, sodium tungstate is dissolved, and after filtration tungstic acid is precipitated by hydrochloric acid.

(2) The mineral is fused with an equal weight of calcium carbonate and one-half of its weight of sodium chloride, and the melt is treated with hot water containing hydrochloric and nitric acids. The tungstic acid remains undissolved.

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[*] See also an interesting discussion of the treatment of tungsten ores, etc., by Van Wegenen, The Chemical Engineer, Vol. IV, 217–232 and 284–297.

(3) The mineral is decomposed by hydrochloric acid (*vid.* Experiment 1).

The Element. *A. Preparation.*[*] Elementary tungsten may be obtained (1) by heating the acid in the presence of hydrogen; (2) by heating the chloride (WCl_6) in the presence of hydrogen; (3) by heating the acid with carbon; (4) by heating the nitride; (5) by passing an electric current *in vacuo* through filaments of an amalgam of tungsten, cadmium, and mercury, the cadmium and mercury being expelled and the tungsten left; (6) by heating the acid with metallic zinc (Weiss).

B. Properties.[*] Tungsten is a very hard powder, ranging in color from gray to brownish black, resembling sometimes tin, sometimes iron. Although unchanged in the air at ordinary temperatures, when heated in finely divided condition it ignites and burns to the oxide (WO_3). Its melting-point is variously given as 2650° (Ruff), 2850° (Weiss), 2900° (v. Wartenburg).[†] It is slowly attacked when heated with sulphuric or nitric acid; and readily attacked by a mixture of nitric and hydrofluoric acids,[‡] forming WF_6 or WOF_4, and by fusion with alkalies and saltpeter. It is acted upon also by dry chlorine at high temperatures. It forms alloys with other metals. The specific gravity of tungsten is from 19.3 to 20.2.

Compounds.[§] *A. Typical forms.* The following compounds of tungsten may be considered typical:

Oxides[‖].........		WO_2		WO_3
Chlorides.........	WCl_2	WCl_4	WCl_5	WCl_6
Oxychlorides......				$WOCl_4$ WO_2Cl_2
Bromides.........	WBr_2		WBr_5	

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[*] See Weiss, Zeitsch. anorg. Chem. LXV, 279.

[†] U. S. Bureau of Standards gives 3400° C.
Jeffries, Eng. and Min. Jour. (1918) 227, gives 3350° C.

[‡] For solubilities *vid.* Ruder, Jour. Amer. Chem. Soc. XXXIV, 387.

[§] See also Rosenheim, Zeitsch. anorg. Chem. LIV, 97.

[‖] Some authorities give three oxides between the dioxide and the trioxide, viz., W_2O_5, W_3O_8, and W_4O_{11}.

Oxybromides				$WOBr_4$ WO_2Br_2
Iodide	WI_2			
Fluoride				WF_6
Double fluorides			$KF \cdot WO_2F + H_2O$	$ZnF_2 \cdot WO_2F_2 + 10H_2O$; etc.
Carbide		WC		
Cyanides *		$K_4W(CN)_8$;$K_3W(CN)_8$		
Boride †				WB_2
Silicide		WSi_2		
Sulphides		WS_2		WS_3
Sulpho salts				R_2WS_4 $R_2WS_2O_2$ R_2WSO_3
Tungstates, many salts of the types				R_2WO_4 (normal) $R_2W_4O_{13}$ (meta) $R_6W_7O_{24}$ (para)

Tungstic trioxide (acid) combines with phosphoric pentoxide, arsenic pentoxide, and silicon dioxide in the following proportions:

$$P_2O_5 : WO_3 :: 1 : 22,\ 1 : 21,\ 1 : 20,\ 1 : 16,\ 1 : 12,\ 1 : 7.$$

$$As_2O_5 : WO_3 :: 1 : 16,\ 1 : 6,\ 1 : 3.$$

$$SiO_2 : WO_3 :: 1 : 12,\ 1 : 10.$$

B. Characteristics. The compounds of tungsten are very similar to those of molybdenum, and are known in several conditions of oxidation (*vid.* Typical Forms), of which the highest is the most stable. The trioxide, (WO_3), united with the bases, forms the largest number of salts, the tungstates. The alkali tungstates are the chief soluble salts. When acted upon by reducing agents, tungstic acid or trioxide may be reduced to the dioxide, (WO_2), the solution becoming blue, then brown. When the solution of a tungstate is acidified, tungstic acid is precipitated. Tungstic sulphide, (WS_3), is obtained under the same conditions as molybdenum sulphide, and is brown.

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* Olsson, Ztschr. anorg. Chem. LXXXVIII, 49; Rosenheim, Ber. Dtsch. chem. Ges. XLVII, 392.

† Wedekind, Ber. Dtsch. chem. Ges. XLVI, 1198.

It dissolves in ammonium sulphide, forming a sulpho salt.

Estimation.* Tungsten is ordinarily weighed as the oxide (WO_3), obtained (1) by igniting ammonium tungstate; (2) by decomposing the alkali tungstates with nitric acid, evaporating to dryness, and extracting with water,—tungstic acid remaining undissolved; (3) by precipitating mercury tungstate and driving off the mercury by means of heat, leaving the acid or oxide; (4) by boiling fused lead tungstate with strong hydrochloric acid,—tungstic acid being precipitated (Brearley, Chem. News LXXIX, 64).

Separation. Tungsten may be separated from the metallic bases and many other elements by the following process: fusion with an alkali carbonate, extraction of the alkali tungstate with water, acidification with nitric acid, evaporation to dryness, and extraction with water,—tungstic acid remaining undissolved.

For the separation of tungsten from molybdenum and vanadium, see those elements. From arsenic and phosphorus tungsten is separated by magnesium mixture (Gooch, Amer. Chem. Jour. I, 412; Gibbs, Amer. Chem. Jour. VII, 337).

From tin the separation may be accomplished (1) by ignition with ammonium chloride, tin chloride being volatilized (Rammelsberg); (2) by fusion with potassium cyanide, the tin being reduced to the metal and the tungsten being converted into a soluble tungstate (Talbot).

EXPERIMENTAL WORK ON TUNGSTEN.

Experiment 1. *Extraction of tungstic acid from wolframite* ($(Fe,Mn)WO_4$). Treat 5 grm. of the finely powdered mineral with about 10 $cm.^3$ of a mixture of equal parts of hydrochloric acid and water, and boil as long as any action seems to take place. Decant the solution, add to the residue about 10 cm.^{3} of a mixture of nitric and hydrochloric acids (aqua regia), and warm. Add more acid if necessary, and continue this treatment until the residue is yellow; filter, and wash with dilute hydrochloric acid and then with water. Warm the yellow mass with ammonium hydroxide as long as any solvent action is observed, and filter. Evaporate the filtrate to dryness and ignite the ammonium tungstate to obtain tungstic acid.

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* For the estimation in ores see Low's Technical Methods of Ore Analysis.

Experiment 2. *Formation of sodium tungstate and metatungstate* (Na_2WO_4 and $Na_2W_4O_{13}$, *typical*). (*a*) Dissolve a little tungstic acid in a solution of sodium carbonate.

(*b*) Dissolve a little tungstic acid in a solution of sodium tungstate.

Experiment 3. *Precipitation of tungstic sulphide* (WS_3), *and formation of the sulpho salt* ($(NH_4)_2WS_4$). (*a*) To a solution of sodium or ammonium tungstate add ammonium sulphide, and acidify with hydrochloric acid.

(*b*) Try the action of hydrogen sulphide upon a soluble tungstate.

(*c*) Try the action of ammonium sulphide upon tungstic sulphide.

Experiment 4. *Precipitation of tungstic acid* (WO_3). Acidify a concentrated solution of a tungstate with hydrochloric or nitric acid and boil. Try the action of nitric and hydrochloric acids upon a tungstate in the presence of tartaric acid.

Experiment 5. *Precipitation of barium, lead, and silver tungstates* ($\overset{\mathrm{I}}{R}_2WO_4$, *typical*). To separate portions of a solution of sodium tungstate acidified with acetic acid add solutions of barium, lead, and silver salts respectively.

Experiment 6. *Reduction of tungstic acid.* (*a*) To a solution of a tungstate (e.g., sodium tungstate) add a solution of stannous chloride. Acidify with hydrochloric acid and warm gently. (*b*) To a solution of a tungstate add zinc and hydrochloric acid and warm gently.

Experiment 7. Salt of phosphorus bead tests. Make a bead of microcosmic salt, and heat it in the oxidizing and reducing flames with a small particle of tungstic acid. Try the effect of a small amount of ferrous sulphate upon the bead heated in the reducing flame.

URANIUM,* U, 238.2.

Discovery. Klaproth, in the year 1789, discovered that the mineral pitch-blende, supposed to be an ore of zinc, iron, or tungsten, contained a "half-metallic substance" differing in its reactions from all three (Crell Annal. (1789) II, 387). This he named Uranium in honor of Herschel's discovery of the planet Uranus in 1781. The body that Klaproth obtained was really an oxide of uranium, as Péligot showed in 1842, when he succeeded in isolating the metal (Ann. de Chim. (1842) V, 5).

Occurrence. Uranium is found combined in a few minerals, most of them rare. Pitch-blende is the most abundant source.

Uraninite (*pitch-blende*), $UO_3 \cdot UO_2 \cdot PbO \cdot N$, etc.,	contains	75–85%	(UO_2+UO_3)
Bröggerite, *vid.* Uraninite,	"	76–79%	"
Cleveite, *vid.* Uraninite,	"	66%	"
Nivenite, *vid.* Uraninite,	"	67%	"
Thorianite, $ThO_2 \cdot U_3O_8$,	"	12–25%	U
Gummite, $(Pb,Ca)U_3SiO_{12} \cdot 6H_2O$?,	"	61–75%	UO_3
Thorogummite, $UO_3 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 6H_2O$,	"	22–23%	"
Pilbarite, $PbO \cdot UO_3 \cdot ThO_2 \cdot 2SiO_2 \cdot 2H_2O+2H_2O$,	"	27.09%	"
Mackintoshite, $UO_2 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 3H_2O$,	"	21–22%	UO_2
Uranophane, $CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$,	"	53–67%	UO_3
Naegite,† silicate,	"	28–29%	UO_2
Uranosphaerite, $(BiO)_2U_2O_7 \cdot 3H_2O$,	"	50–51%	UO_3
Walpurgite, $Bi_{10}(UO_2)_3(OH)_{24}(AsO_4)_4$,	"	20–21%	"
Carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 8H_2O$	"	62–65%	"
Torbernite, $Cu(UO_2)_2P_2O_8 \cdot 8H_2O$,	"	57–62%	"
Zeunerite, $Cu(UO_2)_2As_2O_8 \cdot 8H_2O$,	"	55–56%	"

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* For a discussion of radioactive properties, see Chapter III.

† A Japanese mineral, Chem. Zentr. (1905) I, 763.

Autunite, $Ca(UO_2)_2P_2O_8 \cdot 8H_2O$,	contains	55–62%	UO_3
Uranospinite, $Ca(UO_2)_2As_2O_8 \cdot 8H_2O$	“	59–60%	“
Uranocircite, $Ba(UO_2)_2P_2O_8 \cdot 8H_2O$,	“	56–57%	“
Johannite, sulphate, formula doubtful,	“	67–68%	“
Uranopilite, $CaO \cdot 8UO_3 \cdot 2SO_3 \cdot 25H_2O$,	“	77–78%	“
Uranochalcite, *vid.* Uranopilite,	“	36%	U_3O_4
Zippeite, *vid.* Uranopilite,	“	13–14%	“
Voglianite, *vid.* Uranopilite,	“	12%	“
Uraconite, *vid.* Uranopilite,	“	66–71%	“
Thorite, $ThSiO_4$,	“	1–10%	UO_3
Phosphuranylite, $(UO_2)_3P_2O_8 \cdot 6H_2O$,	“	72–77%	“
Trögerite, $(UO_2)_3As_2O_8 \cdot 12H_2O$,	“	63–64%	“
Rutherfordite, UO_2CO_3,	“	80–84%	“
Uranothallite, $2CaCO_3 \cdot U(CO_3)_2 \cdot 10H_2O$,	“	35–37%	UO_2
Liebigite, $CaCO_3 \cdot (UO_2)CO_3 \cdot 20H_2O$,	“	36–38%	UO_3
Voglite, complex carbonate,	“	37%	UO_2
Hatchettolite, $R(Nb,Ta)_2O_6 \cdot H_2O$,	“	15–16%	UO_3
Fergusonite, $\overset{III}{R}(Nb,Ta)O_4$,	“	0– 8%	UO_2
Sipylite, complex niobate,	“	3– 4%	“
Samarskite, $\overset{II}{R}_3\overset{III}{R}_2(Nb,Ta)_6O_{21}$,	“	10–13%	UO_3
Nohlite, *vid.* Samarskite,	“	14%	UO
Vetinghofite, *vid.* Samarskite,	“	9%	U_2O_3
Ainnerödite, complex,	“	16–17%	UO_2
Hielmite, complex,	“	0– 5%	“
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$,	“	5–12%	“
Polycrase, $\overset{III}{R}(NbO_3)_3 \cdot 2\overset{III}{R}(TiO_3)_3 \cdot 3H_2O$,	“	1–19%	“
Yttrocrasite, complex,	“	2– 3%	“
Blomstrandite, tantalo-niobate,	“	23%	UO
Xenotime, YPO_4,	“	4%	UO_3

Extraction. Uranium salts may be extracted from pitchblende as follows:

(1) The mineral is decomposed with nitric acid, the acid solution is evaporated to dryness, and the mass is extracted with water. The residue, which consists largely of lead sulphate, iron arseniate, and iron oxide, is filtered off, and on evaporation of the solution impure nitrate of uranium crystallizes out, which may be purified by recrystallization (Péligot).

(2) The mineral is decomposed by aqua regia (*vid.* Experiment 1).

The Element. *A. Preparation.* Metallic uranium may be obtained (1) by heating a mixture of the chloride UCl_3 with sodium and potassium chloride in a porcelain crucible surrounded by powdered carbon contained in another crucible (Péligot); (2) by heating the oxide (U_3O_8) with sugar carbon in a carbon tube (Moissan).

B. Properties. Uranium is a somewhat malleable white metal with much the appearance of nickel. Heated in air or oxygen to a temperature of 150°–170° C. it burns to the oxide; at ordinary temperatures the oxidation takes place slowly. Uranium dissolves slowly in cold dilute sulphuric acid, and more rapidly upon the application of heat. It is soluble in nitric and hydrochloric acids. It is attacked by chlorine at 150° C. and by bromine at 240° C. The caustic alkalies have no apparent action upon the element. The specific gravity of uranium is 18.6. Its melting-point is 1850° C.

Compounds.* *A. Typical forms.* The following are typical compounds of uranium:

Oxides†			UO_2		$U_3O_8(UO_2+2UO_3)$	UO_3
Carbonates.......						$UO_2CO_3 \cdot 2K_2CO_3$ $UO_2CO_3 \cdot 2(NH_4)_2CO_3$
Chlorides.........		UCl_3	UCl_4	UCl_5		UO_2Cl_2
Bromides........		UBr_3	UBr_4	UBr_5		UO_2Br_2
Iodide...........			UI_4			
Iodate...........						$UO_2(IO_3)_2$
Fluorides........	UF_2		UF_4 UOF_2		UF_6	UO_2F_2 $UO_2F_2 \cdot NaF$, etc.
Sulphides........	US	U_2S_3	US_2			UOS_2 UO_2S
Sulphates........	$UH(SO_4)_2$		$U(SO_4)_2+4H_2O$			$UO_2SO_4+3\frac{1}{2}H_2O$
Nitrate..........						$UO_2(NO_3)_2+6H_2O$
Nitride..........			U_3N_4			

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* See also Giolitti, Gazz. chim. ital. xxxv [ii], 145, 151, 162, 170; Colani, Ann. Chim. Phys. [8] xii, 59–144 (1907); Mazzucchelli, Atti R. Accad. dei Lincei, Roma [5] xvi [ii], 576; also Chem. Zentr. (1908) i, 218; Lancien, Chem. Zentr. (1908) i, 1763; Aloy, Chem. Zentr. (1907) ii, 883.

† Other oxides less well known than those given above are of the following forms: UO, U_2O_3, U_3O_4, and UO_4.

Boride..........		UB_2
Ferrocyanides....	$UFe(CN)_6$	$(UO_2)_3K_2(FeC_6N_6)_2$
Phosphates, ortho.	$UOHPO_4$	$(UO_2)_5H_2(PO_4)_4$
pyro..	$(UO)_2P_2O_7$	$(UO_2)_2P_2O_7$
meta..	$UO(PO_3)_2$	$UO_2(PO_3)_2$
Arseniate........		$UO_2HAsO_4+4H_2O$

Uranates, of types R_2UO_4, $R_2U_2O_7$, and R_4UO_8.

Peruranates, $(Na_2O_2)_2UO_4 \cdot 8H_2O$; $(PbO)_2UO_4.PbUO_4$.

B. Characteristics. Uranium differs from molybdenum and tungsten in manifesting less marked acidic qualities. The chief classes of salts are the uranyl, in which uranium shows its highest degree of oxidation, corresponding to the oxide UO_3 (e.g., UO_2Cl_2), and the uranous, of which the oxide UO_2 is the type (e.g., UCl_4). The uranyl salts are the more stable and better known. They may be reduced by zinc and hydrochloric acid to the lower condition. The uranous salts are easily oxidized to the higher form. The uranyl salts are, in general, yellow, the uranous greenish. The two conditions of oxidation may be further distinguished by the following reactions: the precipitate resulting from the action of ammonium sulphide upon uranyl salts is reddish brown,—upon uranous salts, light green; the precipitate resulting from the action of potassium ferrocyanide upon uranyl salts is blood-red,—upon uranous salts yellowish green.

Uranates of the types $\overset{I}{R}_2UO_4$ and $\overset{I}{R}_2U_2O_7$ are formed by the combination of the oxide UO_3 with the strong bases.

Estimation.* *A. Gravimetric.* Uranium may be weighed (1) as urano-uranic oxide (U_3O_8), obtained by precipitation of ammonium uranate by means of ammonia, and ignition in air or oxygen; (2) as urano-uranic oxide, precipitated electrolytically by a current of 0.18 ampere and 3 volts at a temperature of 70° C. (Smith and Wallace, Jour. Amer. Chem. Soc. xx, 279; Smith and Kollock, *ibid.*

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* *Vid.* Kern, Jour. Amer. Chem. Soc. xxiii, 685. For the estimation in ores, see Low's Technical Methods of Ore Analysis.

XXIII, 607); (3) as uranous oxide (UO_2), obtained by ignition of urano-uranic oxide in a current of hydrogen; (4) as the pyrophosphate ($(UO_2)_2P_2O_7$), obtained by precipitation by means of ammonium phosphate in the presence of ammonium acetate, and ignition.

B. Volumetric. Uranium may be estimated volumetrically (1) by reduction from the higher (UO_3) to the lower (UO_2) condition of oxidation by means of zinc and sulphuric acid, and oxidation with permanganate, according to the following formulæ (Pulman, Amer. Jour. Sci. [4] XVI, 229):

$$(1)\ UO_2SO_4+Zn+2H_2SO_4=ZnSO_4+U(SO_4)_2+2H_2O;$$
$$(2)\ 2KMnO_4+5U(SO_4)_2+2H_2O=$$
$$2KHSO_4+2MnSO_4+H_2SO_4+5UO_2SO_4;$$

(2) by reduction with titanous sulphate and oxidation with permanganate (Newton and Hughes, Jour. Amer. Chem. Soc. XXXVII, 1711).

Separation.* From the metals which precipitate sulphides with hydrogen sulphide in acid solution, uranium may be separated by hydrogen sulphide. From iron, nickel, and other members of its own group it may be separated by ammonium sulphide in the presence of an excess of sodium or ammonium carbonate, the uranium salt remaining in solution. From the alkalies and alkali earths the separation may be accomplished by means of ammonium sulphide in the presence of ammonium chloride, uranium oxysulphide being precipitated.

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* *Vid.* Kern, Jour. Amer. Chem. Soc. XXIII, 685. For the estimation in ores, see Low's Technical Methods of Ore Analysis.

EXPERIMENTAL WORK ON URANIUM.

Experiment 1. *Extraction of uranium salts from pitch-blende.* Warm 5 grm. of pulverized pitch-blende with aqua regia until the decomposition is complete, and remove the excess of acid by evaporation. Extract with water and boil the solution a few minutes with sulphurous acid to reduce the arsenic acid. When the liquid is at about 60° C., pass hydrogen sulphide through to the complete precipitation of arsenic, copper, lead, bismuth, and tin. Filter, oxidize the filtrate with nitric acid, and precipitate with ammonium hydroxide. Treat the precipitate with hot concentrated ammonium carbonate, filter, and allow the filtrate to cool. The double carbonate of uranium and ammonium will separate. A further precipitate, of crude ammonium uranate, may be obtained by boiling the mother-liquor. Uranium salts may be extracted from carnotite by the method described under Vanadium, Experiment 1, page 114, the sodium hydroxide precipitate being treated with hot concentrated ammonium carbonate, as directed above.

Experiment 2. *Precipitation of sodium, potassium, or ammonium uranate*, ($\overset{\text{I}}{R}_2U_2O_7$, *typical*). To a solution of a uranyl salt add sodium, potassium, or ammonium hydroxide. Note the yellow color of the precipitate and the insolubility in excess of the reagent. Repeat the experiment with hydrogen dioxide present in the solution.

Experiment 3. *Formation of the soluble double carbonates of uranium with sodium or potassium, and uranium with ammonium*, ($UO_2CO_3 \cdot 2\overset{\text{I}}{R}_2CO_3$)· (*a*) To a solution of a uranyl salt add a solution of sodium or potassium carbonate, noting the first and the final effects. Try the result of boiling, and of adding sodium or potassium hydroxide to a separate portion of the clear solution.

(*b*) Try similarly the action of ammonium carbonate upon a uranyl salt in solution. Note the ready solvent action of an excess of the carbonate, and the precipitation of ammonium uranate, ($(NH_4)_2U_2O_7$), on boiling.

(*c*) To a solution of a uranyl salt add hydrogen dioxide and potassium or sodium carbonate. Note the cherry-red color (Aloy).

Experiment 4. *Precipitation of uranyl ferrocyanide,* ($(UO_2)_3K_2(FeC_6N_6)_2$ or $(UO_2)_2FeC_6N_6$). (*a*) To a very dilute solution of a uranyl salt add a little potassium ferrocyanide in solution. Note the red precipitate. This is a delicate test for uranyl salts. The precipitate, which is similar in color to that formed with cupric salts, may be distinguished from copper ferrocyanide by its decomposition on treatment with potassium hydroxide with the formation of yellow insoluble potassium uranate.

(*b*) Try similarly the action of potassium ferricyanide.

Experiment 5. *Precipitation of uranyl phosphate,* (UO_2HPO_4). To a solution of a uranyl salt add a solution of hydrogen disodium phosphate. Try the action of the common acids upon the precipitate.

Experiment 6. *Precipitation of uranyl sulphide,* (UO_2S). (*a*) To a solution of a uranyl salt add ammonium sulphide. Note the dark-brown color of the precipitate, and the insolubility in excess of the reagent.

(*b*) Try the action of hydrogen sulphide upon a uranyl salt.

Experiment 7. *Reduction of uranyl salts.* (*a*) To a solution of a uranyl salt add zinc and sulphuric acid. Note the change of color from yellow to green.

(*b*) Bring about the reduction with magnesium and acid. Test the uranous salt in solution with potassium ferrocyanide and with ammonium sulphide.

Experiment 8. *Bead tests.* Fuse a little of a uranium salt in a borax or sodium metaphosphate bead. Note the yellow color in the oxidizing flame and green color in the reducing flame.

CHAPTER IX.

SELENIUM, Se, 79.2.

Discovery. For some time previous to the discovery of selenium a red deposit had been noticed in the lead chambers used in the manufacture of sulphuric acid at Gripsholm in Sweden. The deposit was present when the sulphur employed had been prepared from pyrites from Fahlun, Sweden, but was seldom observed when the sulphur had been obtained from other sources. At first the unknown substance was supposed to be sulphur. When it was burned, an odor as of decayed cabbage was given off, and this was supposed to be caused by the presence of tellurium sulphide, although no tellurium could be extracted from the material. In 1817 Berzelius, having become a shareholder in the acid works, examined the red deposit, and in a short time he announced the discovery of a new element. Because of its frequent association with tellurium, and its many points of similarity to that element, he named it Selenium, from σελήνη, the *moon* (Annal. der Phys. u. Chem. (1818) XXIX, 229).

Occurrence. Selenium is found usually in combination with the metals, as in the following minerals:

Clausthalite, PbSe,	contains......	27–28%	Se
Tiemannite, HgSe,	"	25–29%	"
Guanajuatite, Bi_2Se_3,	"	24–34%	"
Naumannite, $(Ag_2,Pb)Se$,	"	27–30%	"
Berzelianite, Cu_2Se,	"	39–40%	"
Lehrbachite, $PbSe \cdot HgSe$,	"	24–28%	"
Eucairite, $Cu_2Se \cdot Ag_2Se$,	"	31–32%	"
Zorgite, *vid.* Clausthalite,	"	29–34%	"

Crookesite, $(Cu,Tl,Ag)_2Se$,	contains......	30–33% Se
Onofrite, $Hg(S,Se)$,	"	4– 6% "
Weibullite, $2PbS \cdot Bi_4S_3Se_3$,	"	0–14% "
Chalcomenite, $CuSeO_3 \cdot 2H_2O$,	"	48–49% SeO_2
Tellurium (native), Te,	"	6– 7% Se
Selen-sulphur, $xSe \cdot yS$,	"	35–66% "
Selen-tellurium, $3Te \cdot 2Se$,	"	29–30% "

It is found also in some volcanic lavas, and in anode muds in electrolytic copper refineries.

Extraction. Selenium salts may be extracted from flue-dust by the following methods:

(1) The soluble material is dissolved by treatment with water, and the selenium is extracted from the residue by aqua regia (Berzelius; *vid.* Experiment 1).

(2) The seleniferous material is digested with a solution of potassium cyanide at a temperature of 80°–100° C. until the red color has changed to gray, (KSeCN). The selenium goes into solution and may be precipitated by hydrochloric acid (Pettersson, Ber. Dtsch. chem. Ges. VII, 1719).

(3) The flue-dust or mineral is fused with sodium carbonate, and the selenium is extracted with water as sodium selenide and selenite, (Na_2Se; Na_2SeO_3).

The Element. *A. Preparation.* Selenium in the elementary condition may be prepared by the action (1) of sulphur dioxide, zinc, or iron, upon selenious acid (Berzelius); (2) of hydrochloric acid upon sodium seleno-sulphite (Pettersson); (3) of potassium iodide, sodium thiosulphate, etc., upon selenious acid.

B. Properties. Like sulphur, selenium is known in several allotropic modifications,* and may be either soluble or insoluble in carbon disulphide. In soluble form selenium is a red powder which softens at 50°–60° C., is partly fluid at 100° C. and is completely fused at 250° C. After it has been melted it remains in a plastic condition for a long time and has a metallic luster. Its specific gravity is 4.2 to 4.3. From a warm solution in carbon disulphide the element separates in red, monoclinic, crystalline plates, and from a cold solution in orange-red monoclinic crystals of different type. The specific gravity of these crystalline varieties is 4.4 to 4.5. Selenium insoluble in carbon disulphide may be obtained by allowing the element to cool very slowly after it has been heated to a higher temperature than 130° C., or by allowing the oxygen of the air to act upon selenides in aqueous solution. Under these conditions the element assumes the so-called metallic form, crystallizes in steel-gray hexagonal crystals, and becomes isomorphous with tellurium. Selenium in this form is a poor conductor of electricity, but when heated to about 200°, C. it becomes a good conductor. Metallic selenium melts at 217° C. without previous softening. Its specific gravity is 4.8.

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* For discussions of these modifications, see Saunders, Jour. Phys. Chem. (1900) IV, 423; Marc, Physikalisch-chemischen Eigenschaften des metallischen Selens, pub. by Leopold Voss, Hamburg, 1907; de Coninck, Bull. Acad. roy. Belgique (1907), 365, or Chem. Zentr. (1907) II, 575; Pochettino, Atti Accad. Lincei, Roma [5] XX [1], 428.

Selenium boils at 700° C., yielding a dark-yellow vapor which, when condensed and cooled, assumes a form similar to flowers of sulphur; this is called flowers of selenium. The element is soluble in sulphuric acid, giving a green solution, and is oxidized by nitric acid to selenious acid, (H_2SeO_3). It combines with metals to form selenides. When heated in air or oxygen it burns with a blue flame and goes over to the dioxide, (SeO_2). It is a poor conductor of heat and electricity.

Compounds.* *A. Typical forms.* The following compounds of selenium may be considered typical:

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* Rimini, Gaz. chim. ital. XXXVII [I], 261; Pellini, Atti Accad. Lincei, Roma [5] XV [I], 629, 711; [II], 46; XVIII [II], 211; or Review in Jour. Amer. Chem. Soc. XXIX, 395; Vanino, J. prakt. Chem. XCI, 116; Gutbier, Ztschr. anorg. Chem. LXXXIX, 307.

Oxides		SeO_2	
Fluorides		SeF_4	SeF_6? *
Chlorides	Se_2Cl_2	$SeCl_4$	
		$SeCl_3Br$	
Oxychloride		$SeOCl_2$	
Bromides	Se_2Br_2	$SeBr_4$	
		$SeClBr_3$	
Iodides	Se_2I_2	SeI_4	
Seleno-sulphite	$SeSO_3$		
Alums			$\overset{I}{R}_2Al_2(SeO_4)_4+24H_2O$
Thioselenic acid			H_2SSeO_3
Thioseleniate			K_2SSeO_3
Cyanides	$(CN)_2Se$		
	$(CN)_2Se_3$		
	$H(CN)Se$		
	$K(CN)Se$		
	$\overset{II}{R}(CN)Se_2$		
Nitride	N_2Se		
Phosphides	P_4Se_3		
	P_2Se_5		
Selenides	H_2Se		
	CSe_2		
	$NiSe$		
	Ag_2Se		
	Na_2Se_2, Na_2Se_3,† Na_2SeO_3,‡ $\overset{I}{R}_2SeO_4$		
	K_2Se, etc.		
Acids (selenious and selenic)		H_2SeO_3, H_2SeO_4	
Salts (selenites and seleniates)		$\overset{I}{R}_2SeO_3$,† $\overset{I}{R}_2SeO_4$	

B. Characteristics. The compounds of selenium, as will appear later, closely resemble those of tellurium, both in structure and in behavior toward reagents. They are, however, rather more sensitive to the action of reducing agents, and readily precipitate the red amorphous variety of the element, which tends to become black when heated. Hydrogen selenide is a gas which acts like hydrogen sulphide and hydrogen telluride, and precipitates the selenides ($\overset{I}{R}_2Se$). By the treatment of elementary selenium with nitric acid or aqua regia and evaporation to dryness, selenious oxide, (SeO_2), is formed, which dissolves in water, forming selenious acid, (H_2SeO_3). By the action of powerful oxidizing agents, such as chlorine, bromine, or potassium permanganate, selenious acid may be oxidized to selenic acid, (H_2SeO_4), which is not reduced by sulphur dioxide. These acids form salts of the types $\overset{I}{R}_2SeO_3$ and $\overset{I}{R}_2SeO_4$. By the action of reducing agents, such as sulphur dioxide or ferrous sulphate, red amorphous selenium may be readily precipitated from selenious acid. Two chlorides, (Se_2Cl_2; $SeCl_4$), and the corresponding bromides and iodides are known. When selenium is heated, a characteristic, penetrating odor is given off which has been variously described as like that of garlic, decayed cabbage, and putrid horseradish. This odor is caused by the formation of small amounts of the hydride.

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* Ramsay, Compt. rend. CXLIV, 1196; Lebeau, Compt. rend. CXLV, 190.

† Mathewson, Jour. Amer. Chem. Soc. XXIX, 867.

‡ For selenites of the rare earths see Espil, Compt. rend. CLII, 378.

Estimation. *A. Gravimetric.* Selenium is generally weighed as the element, obtained by treating solutions of its compounds (1) with sulphurous acid in hydrochloric acid solution; (2) with potassium iodide in acid solution (Peirce, Amer. Jour. Sci. [4] 1, 416); (3) with hypophosphorus acid in alkaline solution (Gutbier and Rohn, Zeitsch. anorg. Chem. XXXIV, 448). Other reducing agents may be used (*vid.* Gutbier, Ztschr. anal. Chem. LIV, 193).

B. Volumetric. Selenium may be determined volumetrically (1) by oxidizing selenious acid to selenic by means of standard potassium permanganate in sulphuric acid solution, using an excess of permanganate, and titrating back with oxalic acid (Gooch and Clemons, Amer. Jour. Sci. [3] L, 51); (2) by reducing selenic or selenious acid by means of potassium iodide in hydrochloric acid solution, ($SeO_2 + 4HI = 2H_2O + Se + 2I_2$; $SeO_3 + 6HI = 3H_2O + Se + 3I_2$), and determining by appropriate means the iodine set free (Muthmann and Schaefer, Ber. Dtsch. chem. Ges. XXVI, 1008; Gooch and Reynolds, Amer. Jour. Sci. [3] L, 254); (3) by reducing selenic acid to selenious by boiling with hydrochloric acid, ($SeO_3 + 2HCl = SeO_2 + H_2O + Cl_2$), then passing the free chlorine into potassium iodide, and determining the iodine set free (Gooch and Evans, Amer. Jour. Sci. [3] L, 400); (4) by employing potassium bromide and sulphuric acid instead of hydrochloric acid in (3) (Gooch and Scoville, Amer. Jour. Sci. [3] L, 402); (5) by boiling a solution of selenious acid with sulphuric acid, a known amount of potassium iodide, and an excess of arsenic acid; the reduction of the selenious acid will decrease the reduction of arsenic acid; the quantity of arsenious acid present at the close of the action may be measured, after neutralization with potassium bicarbonate, by standard iodine (Gooch and Peirce, Amer. Jour. Sci. [4] I, 31); (6) by the reduction of selenious acid to elementary selenium by means of standard sodium thiosulphate solution in excess in the presence of hydrochloric acid,—the excess of thiosulphate being determined by standard iodine solution (Norris and Fay, Amer. Chem. Jour. XVIII, 703; Norton, Amer. Jour. Sci. [4] VII, 287); (7) by boiling elementary selenium with ammonia and standard silver nitrate solution, acidifying with nitric acid, and determining the excess of silver nitrate by ammonium sulpho-cyanide, with ferric alum as indicator; the quantity of selenium present is calculable from the quantity of silver nitrate used, as is shown in the following equation: $4AgNO_3 + 3Se + 3H_2O = 2Ag_2Se + H_2SeO_3 + 4HNO_3$ (Friedrich, Zeitsch. angew. Chem. XV, 852).

Separation. Selenium is separated, together with tellurium, from other elements by methods given under Tellurium, where the separation of these two elements from each other is also discussed.

EXPERIMENTAL WORK ON SELENIUM.

Experiment 1. *Extraction of selenium from* (1) *flue-dust and* (2) *seleniferous residues from electrolytic refining of copper.* (1) Treat about 25 grm. of the washed flue-dust with aqua regia as long as any evidence of action is observed, and evaporate to dryness. Extract the residue with about 25 cm.^{3} of strong common hydrochloric acid, and filter. To the filtrate add about a gram of dry ferrous sulphate, and warm gently if necessary. Filter off the red amorphous selenium.

(2) Treat about 25 grm. of the residues with strong commercial hydrochloric acid, warm as long as anything appears to dissolve, and filter. Precipitate the selenium as in (1). Save the filtrate to be examined later for tellurium.

Experiment 2. *Preparation of selenium dioxide*, (SeO_2). To a small amount of elementary selenium add nitric acid until the oxidation is shown to be complete by the cessation of the evolution of red fumes (oxides of nitrogen). Evaporate to dryness and warm gently. The white residue is selenium dioxide. Dissolve this in a little water to form selenious acid, (H_2SeO_3).

Experiment 3. *Precipitation of selenites.* (*a*) To a little selenious acid add a few drops of a barium salt in solution. Test the action of hydrochloric acid upon the precipitate.

(*b*) Try the action of cupric sulphate upon a little selenious acid.

(*c*) Try similarly the action of a solution of mercurous nitrate.

Experiment 4. *Formation of selenic acid* (H_2SeO_4). (*a*) To a few cm.^{3} of selenious acid add first a small amount of sulphuric acid and then a solution of potassium permanganate until the purple color is permanent. Bleach by the careful addition of oxalic acid.

(*b*) Pass chlorine gas into water in which some elementary selenium is suspended.

Experiment 5. *Reactions with selenic acid.* (*a*) To a solution of selenic acid formed as in 4 (*b*) add a little barium salt in solution. Note the precipitation of barium selenate ($BaSeO_4$).

(*b*) Try the action of a solution of cupric sulphate upon a solution of selenic acid. Compare with 3 (*b*).

(*c*) To a solution of selenic acid, free from chlorides, add a little mercurous nitrate in solution. Note the precipitate of mercurous selenate (Hg_2SeO_4).

Experiment 6. *Reduction of selenic acid to selenious.* Add to a given volume of selenic acid half as much strong hydrochloric acid and boil to about two thirds of the total volume. Note the evolution of chlorine. Test by starch iodide paper.

Experiment 7. *Precipitation of elementary selenium.* Try the action of the following reducing agents upon dilute selenious acid: sulphur dioxide, hydrogen sulphide, acid sodium sulphite, potassium iodide, stannous chloride, ferrous sulphate.

Experiment 8. *Solvent action of carbon disulphide upon selenium.* To a little dry, washed, amorphous selenium add carbon disulphide. Filter, and allow the filtrate to evaporate.

Experiment 9. *Solvent action of potassium cyanide upon selenium.* To a small amount of the red amorphous selenium add a few $cm.^3$ of a dilute solution of potassium cyanide (poison!), warm gently, and filter. To the filtrate add hydrochloric acid.

Experiment 10. *Behavior of selenium when subjected to heat.* Heat a small amount of elementary selenium on a glass rod. Note the odor, and the color of the flame.

Experiment 11. *Action of strong sulphuric acid upon selenium.* To a small amount of elementary selenium add a few cm.^{3} of strong sulphuric acid and warm. Note the green color. Allow to cool and add water. Note the precipitation of the selenium ($SeSO_3 + H_2O \rightleftarrows H_2SO_4 + Se$).

TELLURIUM, Te, 127.5.[*]

Discovery. Native tellurium, which is quite widely distributed in small quantities, was a puzzle to the early mineralogists. Because of its non-metallic properties and its metallic luster it was known as *aurum paradoxum* and *metallum problematicum.* In 1782 Müller von Reichenstein, after some careful work on this interesting substance, suggested that a peculiar metal might be present. Acting on the suggestion, Klaproth undertook an investigation, and in 1798 he demonstrated that the "metal" was not identical with any known element. He proposed the name Tellurium, from *tellus, earth* (Crell Annal. (1798) I, 91).

Occurrence. Tellurium occurs in combination and also, sparingly, native.

Petzite,[†] $(Ag,Au)_2Te$,	contains..	32–35%	Te
Goldschmidtite, Au_2AgTe_6,	" ..	59–60%	"
Hessite, Ag_2Te,	" ..	37–44%	"

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[*] See Lenher, Jour. Amer. Chem. Soc. XXX, 741, for a review of the work on the homogeneity of tellurium. Marckwald (Ber. Dtsch. chem. Ges. XL, 4730) claims that previous atomic weights have been defective, and gives 126.85 as the result of his work. Later (XLIII, 710) by means of volumetric methods he arrives at 127.6 as the result. Browning and Flint and later Flint (Amer. Jour. Sci. [4] XXVIII, 347; XXX, 209) obtained a value approaching 126.5. Harcourt and Baker (Jour. Chem. Soc. (London) XCIX, 1311) reaffirm 127.5 and Dennis and Anderson (Jour. Amer. Chem. Soc. XXXVI, 882) reach the same conclusion. For a discussion of the whole subject see Pellini, Ueber das Atomgewicht des Tellurs, pub. by Ferd. Enke, Stuttgart, 1915.

[†] Pellini, Gazz. chim. ital. XLV, I, 469.

Empressite, AgTe,	contains..	54–55%	Te
Altaite, PbTe,	" ..	37–38%	"
Coloradoite, HgTe,	" ..	38–39%	"
Melonite, Ni_2Te_3,	" ..	73–76%	"
Kalgoorlite, $HgAu_2Ag_6Te_6$,	" ..	37–56%	"
Sylvanite, $(Au,Ag)Te_2$,	" ..	58–62%	"
Calaverite, $(Au,Ag)Te_2 \cdot AuTe_2$,	" ..	56–58%	"
Krennerite, $(Au,Ag)Te_2 \cdot AuTe_2$,	" ..	38–59%	"
Muthmannite, $(Au,Ag)Te$	" ..	46–47%	"
Nagyagite, $Au_2Pb_{14}Sb_3Te_7S_{17}$,	" ..	15–31%	"
Goldfieldite, $5Cu_2S(Sb,Bi,As)_2(S,Te)_3$	" ..	17%	"
Tapalpite, $3Ag_2(S,Te) \cdot Bi_2(S,Te)_3$?,	" ..	20–24%	"
Von Diestite, $xAg_2Te \cdot yBi_2Te_3$	" ..	34–35%	"
Tetradymite, $Bi_2Te_3S_3$,*	" ..	33–49%	"
Grünlingite, Bi_4TeS_3,	" ..	12–13%	"
Rickardite, $Cu_2Te \cdot 2CuTe$,	" ..	59–60%	"
Joseïte, formula doubtful,	" ..	15–16%	"
Wehrlite, " "	" ..	29–35%	"
Stützite, Ag_4Te?,	" ..	22–23%	"
Tellurite, TeO_2,	" ..	79–80%	"
Montanite, $Bi_2(OH)_4TeO_6$?,	" ..	24–28%	TeO_3
Emmonsite, formula doubtful,	" ..	59–60%	Te
Durdenite, $Fe_2(TeO_3)_3 \cdot 4H_2O$,	" ..	47–64%	TeO_2
Tellurium (native), Te,	" ..	93–97%	Te
Selen-tellurium, $3Te_2Se$,	" ..	70–71%	"

Tellurium is found also in residues from the electrolytic refining of copper, and in flue-dust from smelters working telluride gold ores.

Extraction. Tellurium may be extracted by the following methods:

(1) *From tellurium bismuth* (*tetradymite*). The mineral is mixed with its own weight of sodium carbonate, and oil is added until the mass has the consistency of thick

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* Amadori, Atti accad. Lincei xxiv, II, 200.

paste. This is heated strongly in a well-closed crucible and then extracted with water. The extract, containing sodium sulphide and sodium telluride, (Na_2Te), is separated by filtration from the insoluble matter and left exposed to the air. The tellurium separates as a gray powder. It may be purified by distillation (Berzelius).

(2) *From sylvanite or nagyagite.* The mineral is treated with hydrochloric acid, which dissolves the antimony, arsenic, etc. The residue is dissolved in aqua regia, the excess of acid is removed by evaporation, and the gold is precipitated by ferrous sulphate. After the removal of the gold by filtration the tellurium is precipitated by sulphur dioxide (Von Schrötter).

(3) *From flue-dust containing tellurium.* The material is treated with strong commercial hydrochloric acid (*vid.* Experiment 1).

The Element. *A. Preparation.* Elementary tellurium may be obtained (1) by the action of reducing agents, as sulphurous acid, stannous chloride, or hydrazine upon the salts of tellurium; and (2) by the action of air upon soluble tellurides.

B. Properties. Tellurium is generally considered a non-metal, though Berzelius classed it with the metals. It is known in two conditions: (1) the crystalline, in which the element has a luster like silver, and (2) the amorphous. It is unchanged in the air at ordinary temperatures, but when heated in air or oxygen it burns with a green flame, forming the dioxide (TeO_2). It is not attacked by hydrochloric acid, but is acted upon slowly by concentrated sulphuric acid, with evolution of sulphur dioxide. It is oxidized by nitric acid and aqua regia to tellurous acid, (H_2TeO_3), and is dissolved in hot caustic potash, forming the telluride and tellurite (K_2Te; K_2TeO_3). It combines with metals to form tellurides and some alloys. Like selenium and sulphur, it is a poor conductor of heat and electricity. Its specific gravity is from 6.1 to 6.3.

Compounds. *A. Typical forms.* The following are typical compounds of tellurium:

Oxides	TeO	TeO_2	TeO_3
Chlorides [*]	$TeCl_2$	$TeCl_4$	
Oxychloride		$TeOCl_2$	
Bromides	$TeBr_2$	$TeBr_4$	
Oxybromide		$TeOBr_2$	
Iodides	TeI_2	TeI_4	
Fluoride		TeF_4	
Double fluoride		$TeF_4 \cdot KF$	
Nitrate (basic)		$Te_2O_3(OH)NO_3$	
Sulphite	$TeSO_3$		
Sulphate		$2TeO_2 \cdot SO_3$	
Sulphides (or sulpho salts).		$TeS_2 \cdot 3K_2S$ $TeS_2 \cdot Bi_2S_3$, etc.	
Tellurides	H_2Te,[†] CTe_2[‡] As_2Te_3 K_2Te, etc.		
Acids (tellurous and telluric)		H_2TeO_3 [§]	H_2TeO_4 [‖]
Salts (tellurites and tellurates)		R_2TeO_3	R_2TeO_4

B. Characteristics. The compounds of tellurium closely resemble in general structure those of sulphur and selenium. Hydrogen telluride, (H_2Te), like hydrogen sulphide, is a gaseous substance, and it precipitates metallic tellurides, ($\overset{I}{R}_2Te$), similar to the sulphides. Two oxides, tellurous (TeO_2), and telluric, (TeO_3), are well known,[¶] but, unlike the corresponding oxides of sulphur, they are very sparingly soluble in water. The acids, (H_2TeO_3; H_2TeO_4), may be formed by acidifying solutions of the alkali salts (e.g., Na_2TeO_3 or Na_2TeO_2) which have been formed by the action of the alkali hydroxides upon the oxides (TeO_2; TeO_3). Many tellurites and tellurates, (R_2TeO_3; R_2TeO_4), may be formed by treating the alkali tellurites or tellurates with soluble salts of the various bases. Two chlorides are known, ($TeCl_2$; $TeCl_4$), both of which are decomposed by water. The corresponding bromides and iodides are also known. In general, compounds of tellurium are easily reduced to the element. The reduction, however, is not accomplished quite so readily as in the case of selenium compounds.

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[*] For an extended discussion of the halogen salts see Gutbier, Jour. prakt. Chem. [2] LXXXIII, 145; Ztschr. anorg. Chem. LXXXVI, 169.

[†] Dennis and Anderson, Jour. Amer. Chem. Soc. XXXVI, 882.

[‡] Stock, Ber. Dtsch. chem. Ges. XLIV, 1832.

[§] Lenher, Jour. Amer. Chem. Soc. XXXV, 718.

[‖] Gutbier favors the formula H_6TeO_6. See also Staudenmeier, Zeitsch. anorg; Chem. X, 189; Gutbier, Zeitsch. anorg. Chem. XL, 260; J. prakt. Chem. LXXXV. 321; LXXXVI, 150; Faber, Zeitsch. anal. Chem. XLVI, 277.

[¶] A monoxide, (TeO), also has been described.

Estimation.* *A. Gravimetric.* Tellurium is usually weighed as the element, obtained by treating solutions of tellurium compounds (1) with sulphur dioxide; (2) with hydrazine sulphate in ammoniacal solution (Jannasch, Ber. Dtsch. chem. Ges. XXXI, 2377); (3) with hydrazine hydrate or its salts in acid or alkaline solution (Gutbier, Ber. Dtsch. chem. Ges. XXXIV, 2724); (4) with sulphur dioxide and potassium iodide (Frericks, J. pr. Chem. [2] LXVI, 261); (5) with hypophosphorus acid (Gutbier, Zeitsch. anorg. Chem. XXXII, 295); (6) with grape-sugar in alkaline solution (Stolba, *vid.* Kastner, Zeitsch. anal. Chem. XIV, 142); (7) with acid sodium sulphite or magnesium (*vid.* Experiment 1); (8) with sulphur dioxide and hydrazine hydrochloride (Lenher, Jour. Amer. Chem. Soc. XXX, 387).

It may be weighed also as the sulphate, ($2TeO_2 \cdot SO_3$), obtained by treating elementary tellurium with a mixture of nitric and sulphuric acids and evaporating (Metzner, Ann. Chim. Phys. [7] xv, 203).

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* See Gutbier, Studien über das Tellur, pub. by Hirschfeld, Leipzig, 1902; Mac Ivor, Chem. News, LXXXVII, 17, 162.

B. Volumetric. Tellurium may be estimated volumetrically (1) by the reduction of telluric acid to tellurous by means of potassium bromide in sulphuric acid solution, ($H_2TeO_4 + 2HBr = H_2TeO_3 + H_2O + Br_2$), the bromine being passed into potassium iodide, and the iodine estimated by standard thiosulphate (Gooch and Howland, Amer. Jour. Sci. [3] XLVIII, 375); (2) by the reducing action of strong hydrochloric acid upon soluble tellurates, chlorine being set free and passed into potassium iodide with liberation of iodine, as above; (3) by the action of standard potassium iodide solution upon a solution of tellurous acid containing twenty-five per cent. by volume of strong sulphuric acid, ($H_2TeO_3 + 4H_2SO_4 + 4KI = TeI_4 + 4KHSO_4 + 3H_2O$), tellurous iodide being precipitated as a black, curdy mass, which, when shaken, separates in such a manner that the point when precipitation ceases can easily be detected; the quantity of tellurium present is calculable from the quantity of potassium iodide used (Gooch and Morgan, Amer. Jour. Sci. [4] II, 271); (4) by the oxidation of tellurous acid by means of standard potassium permanganate in acid or alkaline solution (Norris and Fay, Amer. Chem. Jour. XX, 278; Gooch and Peters, Amer. Jour. Sci. [4] VIII, 122).

Separation.* From the elements not easily reduced from their compounds to elementary form, tellurium may be separated in general by the action of sulphur dioxide in faintly acid solution; this precipitates elementary tellurium. From bismuth tellurium is separated by the action of potassium sulphide upon the precipitate thrown down from solutions by hydrogen sulphide,—the tellurium dissolving. From antimony the separation may be accomplished (1) by hydrazine hydrate, the tellurium being precipitated (Gutbier, Zeitsch. anorg. Chem. XXXII, 260); (2) by treatment of a solution of sulpho-tellurite and sulpho-antimonite with 20% hydrochloric acid in the presence of tartaric acid, the tellurium separating out (Muthmann and Schröder, Zeitsch. anorg. Chem. XIV, 433). From silver tellurium is separated by hydrochloric acid, the silver being precipitated; from gold by the action of heat on the two metals, tellurium being volatilized; from mercury by the action of phosphorus acid upon a cold dilute hydrochloric acid solution of the salts, mercurous chloride being precipitated.

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* See Gutbier, Studien über das Tellur.

From selenium tellurium may be separated (1) by hydroxylamine in strong hydrochloric acid solution, the selenium being precipitated (Jannasch and Müller, Ber. Dtsch. chem. Ges. XXXI, 2388); (2) by sulphur dioxide in strong hydrochloric acid solution, selenium being precipitated (Keller, Jour. Amer. Chem. Soc. XIX, 771, and XXII, 241); (3) by fusion of the elements with potassium cyanide in the presence of hydrogen, tellurium being precipitated when air is passed through a solution of the melt; (4) by the action of ferrous sulphate (*vid.* Experiment 1); (5) by the greater volatility of the bromide of selenium (Gooch and Peirce, Amer. Jour. Sci. [4] I, 181); (6) by the action of acetic acid on a solution of an alkali tellurite and selenite, tellurous acid being precipitated (Browning and Flint, Amer. Jour. Sci. [4] XXVIII, 112).

EXPERIMENTAL WORK ON TELLURIUM.

Experiment 1. *Extraction of tellurium from flue-dust, or from waste products from the electrolytic refining of copper.* (*a*) Treat about 10 grm. of the material with strong commercial hydrochloric acid until nothing further dissolves, and filter. To a small portion of the filtrate add ferrous sulphate, and warm gently. The presence of selenium will be indicated by a reddish precipitate. If selenium has thus been shown to be present, take about 5 $cm.^3$ of the original filtrate, precipitate the selenium and tellurium by acid sodium sulphite or by magnesium, wash this precipitate, return it to the remainder of the filtrate, and heat to boiling. The selenium present will be precipitated by the tellurium. Remove the selenium by filtration and set it aside. From the filtrate precipitate the tellurium by acid sodium sulphite or by magnesium (Crane, Amer. Chem. Jour. XXIII, 408).

(*b*) Treat the residues with ammonium hydroxide as long as anything appears to dissolve. Filter, and acidify the filtrate with acetic acid. The tellurous acid is precipitated and the selenious acid remains in solution. The tellurous acid may be further purified by dissolving the precipitate in sodium hydroxide and reprecipitating with acetic acid. Dissolve in hydrochloric acid and precipitate the element as in (*a*) (Browning).

Experiment 2. *Action of strong sulphuric acid upon tellurium.* To a small amount of elementary tellurium add a few $cm.^3$ of strong sulphuric acid and warm. Note the reddish-violet color. This reaction constitutes a good test for tellurium. Allow to cool and add water. (See Selenium, Experiment 11).

Experiment 3. *Preparation of tellurium dioxide,* (TeO_2). To a small amount of elementary tellurium add nitric acid, evaporate to dryness, and heat gently.

Experiment 4. *Formation of an alkali tellurite,* ($\overset{I}{R}_2TeO_3$). Dissolve a little tellurium dioxide in a solution of sodium or potassium hydroxide.

Experiment 5. *Formation of telluric acid,* (H_2TeO_4). (*a*) To a solution of an alkali tellurite add sulphuric acid until the precipitate first formed dissolves. Then add gradually a solution of potassium permanganate until no further bleaching action is noticed. (*b*) To an alkaline solution of an alkali tellurite add hydrogen dioxide and warm.

Experiment 6. *Reduction of telluric acid.* To a solution of telluric acid prepared in the previous experiment add a little potassium bromide and sulphuric acid, and boil. Note the evolution of bromine and the reduction to tellurous acid.

Experiment 7. *Precipitation of tellurous iodide*, (TeI_4). To a solution of an alkali tellurite add sulphuric acid until the precipitate first formed dissolves. Then add a few drops of a solution of potassium iodide. Note the black precipitate.

Experiment 8. *Action of potassium cyanide upon tellurium.* Fuse a small amount of elementary tellurium with potassium cyanide out of contact with the air ($2KCN+Te=K_2Te+(CN)_2$). Extract with water and pass air through the solution. Note the precipitation of tellurium.

Experiment 9. *Precipitation of elementary tellurium.* (*a*) Try the action of the following reducing agents upon separate portions of the filtrate obtained in Experiment 1 (2), Selenium, or of any acid solution containing tellurium: stannous chloride, hydrogen sulphide,* sulphurous acid, magnesium, and acid sodium sulphite.

(*b*) Try the action of an alkali stannite upon a solution of an alkali tellurite.

Experiment 10. *Action of tellurium compounds before the blowpipe.* Heat on charcoal a small amount of a tellurium compound. Note the white sublimate and the green color imparted to the reducing flame.

Experiment 11. *Negative test of tellurium.* Try the action of ferrous sulphate upon an acidified solution of a tellurite.

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* Some authors give TeS_2 or $TeS+S$ as the constitution of the precipitate by hydrogen sulphide (Snelling, Jour. Amer. Chem. Soc. xxxiv, 802).

CHAPTER X.

PLATINUM, Pt, 195.2.

Discovery. In the year 1750 William Watson presented to the Royal Society a communication from William Brownrigg in which was described a "semi-metal called Platina di Pinto" found in the Spanish West Indies. Watson stated that, so far as he knew, no previous mention had been made of this substance except by Don Antonio de Ulloa in the history of his voyage to South America, published in Madrid in 1748 (Phil. Trans. Roy. Soc. (1750) XLVI, 584). However, an earlier discovery is suggested by a statement of Scaliger in 1558, who, in combating the opinion of Cardanus, that all metals are fusible, declared that an infusible metallic substance existed in the mines of Mexico and Darien. As platinum is found in those countries, it is probably the metal referred to. The name Platinum is derived from the Spanish *platina*, the diminutive of *plata, silver*.

Occurrence. Platinum occurs alloyed with the various metals of its group—palladium, osmium, iridium, etc.—and associated with other metals, as iron, lead, copper, titanic iron, etc. It is found chiefly in the Ural Mountains,* associated with chrome iron ore, magnetite, cinnabar, diamonds, and gold, but also in Brazil, Mexico, Borneo, California,†

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* See Duparc, Arch. Sc. phys. et nat. Genève [4] XXXI, 211, 322, 439, 456, 516; Priwoznic, Oesterr. Ztschr. f. Berg- u. Hüttenwesen, LX, 143, 155.

† See Mineral Resources, U. S. (1910), page 773; (1914), 333; Keller, J. Franklin Inst. CLXXIV, 525.

Oregon, Washington, and elsewhere. The Brazilian sources have recently come into prominence, and Hussak (Zeitsch. f. Geo. XIV, 284) has described three types of ore from that country. The first is similar to the Uralian platinum in composition and associated minerals. The second contains no gold or silver, is not associated with magnetite or chromite, and often contains as much as 21% of palladium. It occurs with rutile, xenotime, and diamonds. The third type is free from iron, poor in palladium, and occurs with quartz and tourmaline. Some of the Brazilian ores contain from 73% to 83% of platinum.

Platinum comprises usually from fifty to eighty per cent. of the alloys in which it occurs. It is found combined in the mineral sperrylite, $PtAs_2$, which contains about fifty-three per cent. of the metal.

Extraction. Platinum may be extracted from its alloys by the following methods:

(1) *Fusion process.* The material is fused with sulphide of lead. The iron present combines with the sulphur. The platinum alloys with the lead, while the osmium and iridium do not. The lead-platinum alloy is separated from the mass and cupelled. The platinum is left (Deville and Debray).

(2) *Wet process.* The pulverized alloy is heated in a porcelain dish with aqua regia as long as action continues. The solution obtained is nearly neutralized with calcium hydroxide, and the iron, copper, rhodium, iridium, and part of the palladium separate. After the removal of these, the filtrate is evaporated to dryness and the residue is ignited and treated with water and hydrochloric acid. The platinum, with traces of the platinum metals, remains.

The Element. *A. Preparation.* As extracted from its alloys, platinum is in the elementary condition (*vid.* Extraction).

B. Properties. In its usual form, elementary platinum is a grayish-white metal which is very malleable and ductile, but fusible only in the oxyhydrogen blowpipe flame or by means of the electric current. Nernst[*] has determined its melting-point as 1745° C.,[†] Guntz[‡] has found it somewhat volatile at from 1000° C. to 1300° C., and Moissan[§] has volatilized it in the electric furnace. At no temperature is it oxidized by water or oxygen. Quennessen[||] finds it to be slightly soluble in sulphuric acid in the presence of oxygen, and Marie[¶] states that it is oxidized by acid and alkaline permanganate, by persulphates, chlorates, bichromates, alkaline ferricyanide, and concentrated nitric acid. Berthelot[**] finds it to be acted upon by fuming hydrochloric acid in the presence of light and manganous chloride. It is readily soluble in aqua regia. Platinum is not acted upon by sulphur alone, but if alkalies are present with the sulphur some action takes place. It is attacked also when heated with potassium nitrate. Its specific gravity is 21.48.

Besides the ordinary form, the element platinum is known to exist in two allotropic conditions: (1) spongy platinum, obtained by the ignition of ammonium chloroplatinate, and (2) platinum-black, obtained by reducing acid solutions of platinum salts. In both of these forms platinum condenses gases on its surface.[††]

Compounds. *A. Typical forms.* The following may be regarded as typical compounds of platinum:

Oxides	PtO		Pt_3O_4	PtO_2	PtO_3
Chlorides	$PtCl_2$	$PtCl_3$		$PtCl_4$	
Double chlorides	$PtCl_2 \cdot SrCl_2 + 6H_2O$, etc.			$PtCl_4 \cdot 2AgCl$, etc.	
Bromides	$PtBr_2$			$PtBr_4$	
Double bromides	$PtBr_2 \cdot 2KBr$, etc.			$PtBr_4 \cdot SrBr_2 + 10H_2O$	

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[*] Nernst, Ber. phys. Ges. IV, 48.

[†] U. S. Bureau of Standards gives 1755° C.

[‡] Guntz, Bull. soc. chim. [3] XXXIII, 1306.

[§] Moissan, Compt. rend. CXLII, 189.

[||] Quennessen, Compt. rend. CXLII, 1341.

[¶] Marie, Compt. rend. CXLVI, 475.

[**] Berthelot, Compt. rend. CXXXVIII, 1297.

[††] Sieverts, Ber. Dtsch. chem. Ges. XLV, 221; Ztschr. anorg. Chem. XCII, 329; Phillips, Amer. Chem. J. XVI, 163; Paal, Ber. Dtsch. chem. Ges. XLVIII, 1195, Curtman and Rothberg, Jour. Amer. Chem. Soc. XXXIII, 718.

Iodides	PtI_2	PtI_4
Double iodides		$PtI_4 \cdot 2KI$, etc.
Fluorides	PtF_2	PtF_4
Sulphides	PtS	PtS_2
Oxysulphide		$PtOS$
Sulpho salts		R_2PtS_6
Sulphites		$PtSO_3 \cdot \overset{I}{R}_2SO_3$; $PtSO_3 \cdot 2\overset{I}{R}Cl$
Nitrites		$\overset{I}{R}_2(NO_2)_4Pt$
Iodonitrites		$\overset{I}{R}_2(NO_2)_2I_2Pt$
Cyanide	$Pt(CN)_2$	
Hydro-platino-cyanic acid	$H_2Pt(CN)_4$	
Platino-cyanides *	$\overset{I}{R}_2Pt(CN)_4$; $\overset{II}{R}Pt(CN)_4$, typical	
Chloroplatinic acid		H_2PtCl_6
Chloroplatinates †		$\overset{I}{R}_2PtCl_6$; $\overset{II}{R}PtCl_6$, typical
Chloroplatinite †	K_2PtCl_4	

B. Characteristics. The compounds of platinum may be divided into two classes, of which the platinous and platinic oxides, (PtO; PtO_2), serve as types. The salts of the lower condition of oxidation are usually colorless or reddish brown; they give with hydrogen sulphide or ammonium sulphide a dark-brown precipitate of platinous sulphide, (PtS), which is soluble in ammonium sulphide. They are decomposed at red heat, and are slowly reduced to metallic platinum when boiled with ferrous sulphate. The salts of the higher condition of oxidation have a yellow or brown color, and like the platinous salts they are decomposed at red heat. Metals in general and organic matter precipitate platinum from solutions of platinic salts. The brownish-gray platinic sulphide, (PtS_2), is precipitated by the action of hydrogen sulphide upon a solution of chloroplatinic acid, (H_2PtCl_6); this sulphide dissolves slowly in ammonium sulphide. Salts of potassium and ammonium act upon chloroplatinic acid precipitating the corresponding salts of that acid, ($\overset{\text{I}}{R}_2PtCl_6$). When platinous chloride dissolves in potassium cyanide, platinum potassium cyanide is formed, ($K_2Pt(CN)_4+4H_2O$). Many salts of this type are known (Levy, Proc. Roy. Soc. XXVIII, 91).

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* *Vid.* Tschugajew, Ber. Dtsch. chem. Ges. XLVII, 2643.

† *Vid.* Zappi, Chem. Abs. X, 1307.

The platinum-ammonium compounds comprise a large number of complex salts* of the following types:

(*a*) The platosamines, $PtR_2(NH_3)_4$; $PtR_2(NH_3)_3$; $PtR_2(NH_3)_2$; $PtR_2(NH_3)$; and (*b*) the platinamines, $PtR_4(NH_3)_4$; $PtR_4(NH_3)_3$; $PtR_4(NH_3)_2$; $PtR_4(NH_3)$.

In the above formulæ R may stand for OH, Cl, Br, I, or NO_3. These compounds are formed by the action of ammonia upon the platinum salts.

Potassium iodide gives a red-brown color to very dilute solutions of platinum salts.

Estimation. *A. Gravimetric.* Platinum is generally weighed as the metal, obtained (1) by precipitation from solutions of compounds by means of appropriate reducing agents, such as formic acid, alcohol in alkaline solution, or magnesium (Atterberg, Chem. Ztg. XXII, 538); (2) by precipitation of the sulphide and ignition; (3) by precipitation of ammonium or potassium chloroplatinate, and decomposition by heat into the metal and the volatile or soluble alkali chloride.

B. Volumetric. Platinum may be estimated volumetrically by reducing the tetrachloride by means of potassium iodide, ($PtCl_4+4KI=PtI_2+I_2+4KCl$), and determining by standard sodium thiosulphate the iodine thus liberated (Peterson, Zeitsch. anorg. Chem. XIX, 59).

Separation. From most other elements platinum may be separated by the action of reducing agents in precipitating the metal from solutions. From the metals with which it is most often found associated it may be separated by the following methods: from gold (1) by the action of ammonium chloride upon the chlorides, ammonium chloroplatinate being precipitated; (2) by the action of hydrogen dioxide and sodium hydroxide upon cold solutions, the gold being precipitated (Vanino and Seeman, Ber. Dtsch. chem. Ges. XXXII, 1968); (3) by the action of oxalic acid or ferrous salts, gold being again precipitated (Hoffmann and Krüss, Zeitsch. anal. Chem. XXVII, 66; Bettel, Chem. News LVI, 133); from silver by heating the metals with dilute sulphuric acid, silver dissolving (Steinmann, Schweiz. Wchschr. f. Chem. u. Pharm. XLIX, 441, 453); from mercury by ignition of the metals, mercury being volatilized.

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* See Werner, Ber. Dtsch. chem. Ges. XL, 15; Rosenheim, Zeitsch. anorg. Chem. XLIII, 34; Kirmreuther, Ber. Dtsch. chem. Ges. XLIV, 3115; Chugaev, Compt. rend. CLXII, 43.

The separation of platinum from the other platinum metals is so involved with the separation of these from each other that the whole subject will be briefly considered in this place. The following methods have been suggested. (1) The ore is first treated with chlorine water, which extracts the gold, then with dilute aqua regia, which dissolves the platinum, palladium, and rhodium. From this solution the platinum is precipitated by ammonium chloride and alcohol; and from the filtrate, after neutralization with sodium carbonate, the palladium is precipitated as the cyanide by mercury cyanide. The residue from the aqua regia treatment, containing osmium, iridium, and ruthenium, is heated in air. Osmium is volatilized as the tetroxide, ruthenium sublimes as the dioxide, and iridium is left (Pirngrüber, J. B. (1888), 2560; Wyatt, Eng. and Min. J. XLIV, 273). (2) A neutral or acid solution of the platinum metals, gold, and mercury, containing chlorine, is treated with dilute nitric acid and heated to boiling in a retort; osmic tetroxide distils. The solution is cooled, and shaken with ether, which withdraws the chloride of gold. After the removal of the ether and gold by means of a separating funnel the remaining solution is treated with ammonium acetate and boiled with formic acid. This treatment precipitates all the metals, which are then heated in a current of hydrogen to volatilize the mercury. The remaining metals are mixed with sodium chloride and heated with moist chlorine, and the mass is extracted with water. If there is any residue at this point it will probably be found to be iridium and ruthenium. The solution is treated with concentrated ammonium chloride as long as any precipitate forms. This precipitate consists of the double chlorides of ammonium with platinum, iridium, and ruthenium respectively, palladium and rhodium remaining in solution. The precipitate is dissolved in warm water and treated with hydroxylamine, which reduces the iridium and ruthenium to the condition of the sesquichlorides; upon the addition of ammonium chloride platinum is precipitated as the chloroplatinate. The hydroxylamine filtrate is evaporated, the residue is heated in the presence of hydrogen and fused with potassium hydroxide and nitrate, the mass is cooled and extracted with water. Ruthenium dissolves as potassium ruthenate, (K_2RuO_4), and iridium remains as the hydrate, ($Ir(OH)_3$). The solution containing rhodium and palladium is evaporated slowly to dryness in the presence of an excess of ammonia, and the residue is dissolved in the smallest possible amount of a warm, dilute ammoniacal solution. Upon cooling, the rhodium separates as a complex chloride, ($Rh(NH_3)_5Cl_3$), and the palladium remains in solution (Mylius* and Dietz, Ber. Dtsch. chem. Ges. XXXI, 3187). (3) Gold is removed by means of dilute aqua regia. By treatment with concentrated aqua regia platinum, palladium, rhodium, ruthenium, and part of the iridium are then dissolved, while an insoluble alloy of osmium and iridium in the form of grains or plates remains. This alloy is mixed with sodium chloride and the mixture is heated in a tube with chlorine. Osmium tetroxide, (OsO_4), distils, and sodium-iridium chloride, (Na_2IrCl_6), remains (Wöhler, Pogg. Annal. XXXI, 161). To the solution of the other platinum metals in aqua regia ammonium chloride is added. The precipitate, consisting of the double salts of platinum and iridium, may by ignition be converted into iridium-bearing platinum sponge (used in the manufacture of platinum vessels). To the filtrate iron or copper is added, which throws down the palladium, rhodium, and ruthenium as a metallic powder. From this mixture palladium and the iron or copper are dissolved by nitric acid, and the solution is then shaken with mercury, which removes the palladium (von Schneider, Liebig Annal. v, 264, suppl.). The mixture of rhodium and ruthenium remaining is heated with sodium chloride at low redness in a current of chlorine and the mass is extracted with water. This liquid is boiled with potassium nitrite and enough potassium carbonate to make the solution faintly alkaline. It is then evaporated to dryness and the residue is pulverized and extracted with absolute alcohol. The rhodium remains undissolved as a double nitrite of potassium and rhodium, $(K_6Rh_2(NO_2)_{12}$, while the ruthenium dissolves, also as a double nitrite with potassium, $(Ru(NO_2)_6 \cdot 6KNO_2)$.

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* *Vid.* also Mylius and Mazzucchelli, Ztschr. anorg. Chem. LXXXIX, 1; Korfman, Chem. Abs. IX, 2629.

Platinum may be separated from palladium (1) by the action of warm dilute nitric acid upon the metals, palladium dissolving; (2) by the action of a strong solution of ammonium chloride and alcohol upon the double potassium salts, the palladium salt being soluble (Cohn and Fleissner, Ber. Dtsch. chem. Ges. XXIX, R. 876); from iridium (1) by electrolysis, the platinum being precipitated (Smith, Amer. Chem. Jour. XIV, 435); (2) by the action of potassium nitrite, sodium carbonate, and boiling water upon the double potassium salts, iridium being reduced to the condition of the sesquichloride and dissolved (Gibbs, Amer. Jour. Sci. [2] XXXIV, 347); from osmium by heating in the presence of oxidizing material, osmium tetroxide being formed and volatilized; from ruthenium by treating potassium chloroplatinate and the corresponding ruthenium salt with cold water, the ruthenium salt dissolving (Gibbs, *loc. cit.*); from rhodium (1) by the method described for the separation from ruthenium; or (2) by the action of concentrated solutions of the alkali chlorides upon these salts, the rhodium dissolving (Gibbs, *loc. cit.*).

A method of separation proposed by Leidie and Quennessen (Bull. Soc. Chim. XXVII, (1902) 181), will be found outlined in Table IX, page 226.

EXPERIMENTAL WORK ON PLATINUM.

Experiment 1. *Preparation of chloroplatinic acid from laboratory residues.* Boil the residues consisting of potassium chloroplatinate, etc., with a solution of sodium carbonate and add a little formic acid or formate in solution. The platinum is deposited as a black powder. Wash the powder, first with hot water, then with hot hydrochloric acid; dry it, dissolve it in aqua regia, and evaporate the liquid until the point of crystallization is reached, adding a little hydrochloric acid from time to time to remove the nitric acid, and some chlorine water to convert any platinous acid to the platinic condition.

Experiment 2. *Precipitation of the chloroplatinates of ammonium, potassium, cæsium, rubidium, and thallium,* ($\overset{I}{R}_2PtCl_6$). To separate portions of a solution of chloroplatinic acid add salts of ammonium, potassium, cæsium, rubidium, and thallium in solution. Note the comparative insolubility of the new compounds in water and in alcohol.

Experiment 3. *Formation of chloroplatinous acid.* To a solution of chloroplatinic acid add a little stannous chloride. Note the darkening of the color. Add a little potassium or ammonium salt in solution. Note the absence of precipitation.

Experiment 4. *Precipitation of platinic sulphide,* (PtS_2). To a solution of chloroplatinic acid add a little hydrogen sulphide, and warm. Try action of ammonium sulphide on PtS_2.

Experiment 5. *Precipitation of elementary platinum.*

(*a*) To a solution of a platinum salt add a few drops of a solution of hydrazine sulphate ($N_2H_4 \cdot H_2SO_4$) and warm.

(*b*) Try the action of zinc on a solution containing platinum.

(*c*) Try the action of oxalic acid upon a platinum salt in solution. Note the absence of precipitation.

Experiment 6. *Action of acids upon platinum.* Try separately the action of strong hydrochloric and nitric acids upon metallic platinum. Note the effect of a mixture of the two acids upon the metal.

Experiment 7. *Test for platinum in solution.* To a very dilute solution of a platinum salt free from chlorine add a small crystal of potassium iodide. Note the color.

Experiment 8. "*Glow test*" *for platinum.** Dip the end of a very small piece of asbestos paper into 1 cm.^{3} of chloroplatinic acid, heat the asbestos to redness, and repeat the process until the liquid is completely absorbed. Then, before the asbestos cools, hold it in a current of illuminating gas.

THE PLATINUM METALS (OTHER THAN PLATINUM).

Occurring almost invariably associated with platinum and usually alloyed with it are small quantities of certain rare elements which, together with platinum, comprise the group of so-called Platinum Metals. These very rare elements are the following:

Palladium, Pd, 106.7	Osmium, Os, 190.9
Iridium, Ir, 193.1	Rhodium, Rh, 102.9
Ruthenium, Ru, 101.7	

Discovery. In 1803, in the course of the purification of a considerable quantity of crude platinum, Wollaston isolated a new metal which he named Palladium, in honor of the discovery by Olbers of the planetoid Pallas. The newly discovered element was brought to the attention of scientists anonymously through a dealer's advertisement, which offered "palladium or new silver" for sale. Much discussion as to the nature of the substance ensued, Chenevix, in particular, holding it to be an alloy of platinum and mercury. In 1805 Wollaston confessed to the discovery and naming of the metal (Phil. Trans. Roy. Soc. (1803) XCIII, 290; ibid. (1805) XCV, 316; Nicholson's J. (1805) X, 204).

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* This test applies also to Pd, Ir, and Rh. It is stated that under proper conditions .002 mg. of Pt can be detected (Curtman and Rothberg, Jour. Amer. Chem. Soc. XXXIII, 718).

The same year that palladium was discovered, Smithson Tennant found that "the black powder which remained after the solution of platina did not, as was generally believed, consist chiefly of plumbago, but contained some unknown metallic ingredients." In 1804 he presented to the Royal Society as the result of his study a communication announcing the discovery of two new metals, Iridium, named "from the striking variety of colors which it gives while dissolving in marine acid," and Osmium, so called because of the penetrating odor (*οσμή, odor*) of the acid obtained from the oxidation of the element when it is heated in a finely divided condition (Phil. Trans. Roy. Soc. (1804) XCIV, 411).

A few days after Tennant's communication, Wollaston announced the discovery of an element in the "fluid which remains after the precipitation of platina by sal ammoniac," and suggested the name Rhodium (*ῥόδιος, rose-like*), "from the rose color of a dilute solution of the salts containing it" (Phil. Trans. Roy. Soc. (1804) XCIV, 419).

In 1826 Osann claimed the discovery of three new elements in platinum alloys. These he named Ruthenium, Polinium, and Pluranium (Pogg. Annal. VIII, 505; Amer. Jour. Sci. XVI, 384). Later he withdrew the claim. In 1844 Claus found that there was an unknown metal in the mixture of substances which had been called by Osann "ruthenium oxide," and for it he retained the name ruthenium, derived from Ruthenia, i.e. Russia, where the substance was first found (Pogg. Annal. LXIV, 192, 208; Amer. Jour. Sci. XLVIII, 401).

Late in the year 1911 French (Chem. News CIV, 283) announced the discovery of an element associated with the platinum metals in the dike rocks of the Nelson district in British Columbia. It had the characteristics of a noble metal and was called by him Canadium. Patterson (Chem. News CV, 84), in discussing this discovery, calls attention to the fact that palladium forms alloys with many metals, and that these alloys behave very differently from palladium and resemble elementary substances.

Occurrence. The very rare platinum metals, as has been already stated, are found in general in platinum-bearing material. Palladium and iridium sometimes occur native; the others always in alloys or in combination.

		% Pd	% Os	% Ir	% Rh	% Ru
Native platinum	contains	0.1–3.1		traces–4.2	traces	0.2–3.4
“ iridium	“	0.4–0.8		27–76.8		*circa* 7
Palladium gold	“	5–10				
Iridosmine	“		17–48	40.7	5.5–12.3	0.2–6
Laurite, RuS_2	“		*circa* 3			65
Rhodium gold	“				34–43	

Extraction. For methods of extraction of the very rare platinum metals see Extraction and Separation of Platinum.

The Elements. I. PALLADIUM. *A. Preparation.* Elementary palladium may be obtained (1) by heating the potassium double chloride with hydrogen (Roessler); (2) by heating the iodide with hydrogen; and (3) by heating the chloride or cyanide.

B. Properties. Palladium is a ductile, malleable, white metal which looks like platinum. It may be partially oxidized before the oxyhydrogen blowpipe. It is soluble in strong nitric, hydrochloric, and sulphuric acids, and easily soluble in aqua regia. It fuses at a lower temperature than any other of the platinum metals, 1549° C. (U. S. Bureau of Standards). In spongy form it has the power of absorbing gases.* Its specific gravity is 11.4–11.8. It may be distinguished from the other platinum metals by the comparative ease with which it dissolves in nitric acid.

II. OSMIUM. *A. Preparation.* The element osmium may be prepared (1) by heating the amalgam in the presence of hydrogen (Berzelius); (2) by heating the sulphide in a closed coke crucible; (3) by passing the vapor of the tetroxide mixed with carbon dioxide and carbon monoxide through a heated porcelain tube; (4) by passing the vapor of the tetroxide through a heated porcelain tube containing finely divided carbon (Deville and Debray); (5) by igniting osmyldiamine chloride, ($Os(NH_3)_4O_2Cl_2$), in a current of hydrogen.

B. Properties. Osmium, the heaviest of the platinum metals, is a bluish substance, crystals of which are harder than glass. In the compact form it is insoluble in all acids and in aqua regia, and is rendered soluble only by fusion with nitrates. The amorphous modification is slowly soluble in nitric acid and in aqua regia. The specific gravity of the compact and amorphous modifications is 21.3; of the crystalline form 22.4. Osmium, like the other platinum metals, has been volatilized in the electric furnace (Moissan, Compt. rend. CXLII, 189); it is, however, refractory.† Its melting-point is 2700° C.

III. IRIDIUM. *A. Preparation.* Metallic iridium may be obtained (1) by heating iridium-ammonium chloride, and (2) by heating iridium-potassium chloride with sodium carbonate.

B. Properties. Iridium, a hard, brittle metal, resembles silver and tin in appearance. The ignited form is insoluble in all acids and in aqua regia. The element is partially oxidized, however, by fusion with sodium nitrate, and the fused mass may be dissolved by boiling it with aqua regia. In spongy form iridium has the specific gravity of 15.86; after fusion the specific gravity is 21–22. It has the property of absorbing gases.*

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* The explosive condition of the platinum metals is explained by the property, common to these metals, of occluding hydrogen and oxygen. When heated in nitrogen or out of contact with the air they tend to lose their explosive character. Ruthenium, however, is not changed by this treatment (Cohen and Strengers, Z. physik. Chem. LXI, 698). *Vid.* also Sieverts, ibid. LXXXVIII, 451; Halla, ibid. LXXXVI, 496; Curtman and Rothberg, Jour. Amer. Chem. Soc. XXXIII, 718.

† For a discussion of the volatility of the platinum metals, see Crookes, Proc. Roy. Soc. LXXXVI, 461.

IV. Rhodium. *A. Preparation.* Elementary rhodium may be prepared (1) by heating ammonium-rhodium sesquichloride; (2) by heating rhodium sesquichloride and sodium in a current of hydrogen; (3) by heating rhodium sulphide to a white heat; and (4) by allowing reducing agents, as formic acid, zinc, iron, alcohol in alkaline solution, hydrogen, etc., to act upon soluble salts.

B. Properties. Rhodium is a grayish-white metal which has the appearance of aluminum. When pure it is almost absolutely insoluble in acids and in aqua regia, but when alloyed it may be dissolved in aqua regia. It is fusible before the oxyhydrogen blowpipe, but more difficultly than platinum. It has the property of absorbing hydrogen.* Of all the platinum metals rhodium is most easily attacked by chlorine. Its specific gravity is 11–12. Its melting-point is 1950° C.

V. Ruthenium. *A. Preparation.* The element ruthenium may be obtained (1) by heating the oxide with illuminating-gas, and (2) by heating ruthenium-ammonium-mercury chloride.

B. Properties. Ruthenium is a hard, brittle metal, dark gray to black in color. It is almost completely insoluble in acids and in aqua regia; and osmium alone, of all the platinum metals, is more difficultly fusible. It may be slightly oxidized by fusion with caustic potash and oxidized to a greater degree by fusion with potassium nitrate. The specific gravity of the crystalline form is

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* See Curtman and Rothberg, Jour. Amer. Chem. Soc. XXXIII, 718.

12.26; of the melted form 11.4; and of the porous form 8.6. Its melting-point is 2450° C. ?

Compounds.* *A. Typical forms.* The following compounds of the platinum metals may be considered typical:

Oxides.	Pd_2O				
	PdO	OsO	IrO?	RhO	RuO
	Pd_2O_3 †	Os_2O_3	Ir_2O_3	Rh_2O_3	Ru_2O_3
	PdO_2	OsO_2	IrO_2†	RhO_2	RuO_2
		(OsO_3) ‡			(RuO_3) ‡
		OsO_4			RuO_4
					(Ru_2O_7) ‡
Chlorides.......	$PdCl$				
	$PdCl_2$	$OsCl_2$	$IrCl_2$	$RhCl_2$	$RuCl_2$
		$OsCl_3$	Ir_2Cl_6	Rh_2Cl_6	Ru_2Cl_6
	$PdCl_4$	$OsCl_4$	$IrCl_4$		$RuCl_4$
Bromides......	$PdBr_2$				
			Ir_2Br_6		
	$PdBr_4$		$IrBr_4$		
Iodides........	PdI_2				
			Ir_2I_6?	Rh_2I_6	Ru_2I_6
			IrI_4		
Sulphides......	Pd_2S				
	PdS		IrS	RhS	
			Ir_2S_3	Rh_2S_3	Ru_2S_3
	PdS_2	OsS_2	IrS_2		RuS_2
					RuS_3
		OsS_4			
Sulphates......	$PdSO_4$		$Ir_2(SO_4)_3$ §		
				$Rh_2(SO_4)_3$	
					$Ru(SO_4)_2$
Sulphites.......	$PdSO_3 \cdot 3Na_2SO_3$	$OsSO_3$			
			$Ir_2(SO_3)_3$	$Rh_2(SO_3)_3$	

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[*] Gutbier, Ber. Dtsch. chem. Ges. XLIII, 3228, 3234; XLIV, 306, 308; XLVII, 236; J. prakt. Chem. XCI, 103; Delépine, Compt. rend. CLVIII, 264; Fritzman, J. Russ. Phys. Chem. Soc. XLVII, 588; Peters, Ztschr. anorg. Chem. LXXXIX, 191; Tschugajew, Ber. Dtsch. chem. Ges. XLVII, 2446; Gutbier, Ztschr. anorg. Chem. LXXXIX, 313, 333, 340, 344; Barbieri, Atti R. Accad. dei Lincei, Roma [5] XXIII, I, 334; Fraenkel, Monatshefte Chem. XXXV, 19; Ramberg, Ber. Dtsch. chem. Ges. XLVI, 1696, 3886; Wöhler, Ber. Dtsch. chem. Ges. XLVI, 1577, 1591, 1720; Ruff, ibid. XLVI, 920.

[†] Wöhler, Zeitsch. anorg. Chem. LVII, 323, 398.

[‡] This oxide is known only in combination.

[§] Also alums, see Marino, Zeitsch. anorg. Chem. XLII, 213; complex oxalates, see Gialdini, Atti R. Accad. dei Lincei, Roma [5] XVI [II], 648, or Chem. Zentr. (1908) I, 107.

Sulpho salts....	$R_2Pd_3S_4$ R_2PdS_3				
Nitrites.......	$Pd(NO_2)_2\cdot 2KNO_2$	$Os(NO_2)_3$*	$Ir_2(NO_2)_6\cdot$ $6HNO_2$	$Rh_2(NO_2)_6\cdot$ $6RNO_2$	$Ru_2(NO_2)_6$ $6RNO_2$
Nitrates......	$Pd(NO_3)_2$			$Rh_2(NO_3)_6$	
Acids and correspond'g salts...	H_2PdCl_4; † $\overset{I}{R}_2PdCl_4$				
		H_3OsCl_6; $\overset{I}{R}_3OsCl_6$		$\overset{I}{R}_4RhCl_7$; $\overset{I}{R}_3RhCl_6$ §	H_2RuCl_5‡
	H_2PdCl_6; $\overset{I}{R}_2PdCl_6$	H_2OsCl_6; $\overset{I}{R}_2OsCl_6$	$\overset{I}{R}_2IrCl_6$		H_2RuCl_6

Characteristics. I. PALLADIUM. The compounds of palladium resemble those of platinum, both in form and in general characteristics. As in the case of platinum, palladium combines with ammonia to form complex salts, and an oxide, (PdO), forms salts with sulphur dioxide and with nitrogen trioxide, (N_2O_3). In general the salts are quite easily reduced to the metal by heating; their solutions resemble a solution of platinic chloride in color. Two oxides, (PdO; PdO_2), are well known, of which the lower forms the more stable compounds. These compounds give a yellowish-brown precipitate with potassium hydroxide. Solutions of palladium salts give with mercuric cyanide a yellowish-white precipitate, ($Pd(CN)_2$); with potassium iodide a black precipitate, (PdI_2), which is soluble in excess of the reagent; and with hydrogen sulphide also a black precipitate, (PdS), insoluble in ammonium sulphide.

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[*] See also Wintrebert, Compt. rend. CXL, 585.

[†] See also Gutbier, Ber. Dtsch. chem. Ges. XXXVIII, 23; XXXIX, 4134; XL, 690; Zeitsch. anorg. Chem. XLV, 166, 243; XLVII, 23.

[‡] See also Howe, Jour. Amer. Chem. Soc. XXVI, 543, 942; Gutbier, Zeitsch. anorg. Chem. XLV, 166, 243; XLVII, 23; Ber. Dtsch. chem. Ges. XXXVIII, 2105, 2885.

[§] See also Gutbier, Ber. Dtsch. chem. Ges. XLI, 210.

Mercuric cyanide and potassium iodide are often used as tests for palladium.

II. Osmium.* Compounds of osmium are known in five degrees of oxidation. The lowest three oxides, (OsO; Os_2O_3; OsO_2), are basic in character, the fourth,† (OsO_3), is acidic, and the fifth, (OsO_4), is also acidic, but it forms no salts. Three chlorides, ($OsCl_2$; $OsCl_3$; $OsCl_4$), are known, corresponding to the lowest oxides. The metals sodium, potassium, and barium form salts of the type $\overset{\text{I}}{R}_2OsO_4$. These salts are readily decomposed, especially by acids, and form the dioxide and the tetroxide. When osmium compounds are heated in the air with oxidizing agents, or are melted with potassium nitrate, the tetroxide is obtained. It is volatile when heated, highly corrosive, and disagreeable like chlorine. It is soluble in water and is reduced by reducing agents. From potassium iodide it frees iodine, and with formic acid to which potassium hydroxide has been added it gives a violet color. With ferrous sulphate it precipitates black osmium hydroxide, ($Os(OH)_4$), and with hydrogen sulphide it brings down the brownish-black sulphide (OsS_4), which is insoluble in ammonium sulphide.

III. Iridium.‡ The compounds of iridium exist chiefly in three conditions of oxidation, of which the di-, tri-, and tetrachlorides may serve as types, ($IrCl_2$; Ir_2Cl_6; $IrCl_4$). The iridium compounds are reduced to the metal when mixed with sodium carbonate and heated in the outer flame of a Bunsen burner. The alkali double chlorides with iridous chloride, ($IrCl_2$), are in general soluble in water. Solutions of iridium salts in the lowest condition of oxidation give with potassium hydroxide a greenish precipitate, which tends to darken when boiled. Reducing agents, as sodium formate, precipitate metallic iridium, and hydrogen sulphide precipitates from the warmed solution a brown iridium sulphide (IrS). By means of oxidizing agents, solutions of iridous salts may be converted into the highest condition of oxidation. From solutions of this latter type potassium hydroxide throws down a dark-brown precipitate of potassium-iridium chloride, ($IrCl_4 \cdot 2KCl$), and hydrogen sulphide precipitates slowly a brown sulphide, (Ir_2S_3). The greater number of iridium compounds are easily reduced by hydrogen on being heated. The presence of iridium may be detected by the blue color developed when the compound is heated with concentrated sulphuric acid to which ammonium nitrate has been added.

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* See also Ruff, Zeitsch. anorg. Chem. LXV, 429; Gutbier, Ber. Dtsch. chem, Ges. XLIII, 3228, 3234; XLIV, 306, 308.

† Known only in salts.

‡ For recent work on iridium compounds see Gutbier, Ber. Dtsch. chem. Ges, XLII, 3905, 4770; Delépine, Vezes and Duffour, Bull. Soc. Chim. [4],V, 869, 872, 1084; VII, 507, 512; IX, 710, 771; Compt. rend. CLII, 1393, 1591.

IV. RHODIUM. Although three oxides of rhodium are known and described, (RhO; Rh_2O_3; RhO_2), salts of only two conditions of oxidation are generally found; of these the di- and trichlorides are types, ($RhCl_2$; Rh_2Cl_6). From solutions of rhodium salts reducing agents precipitate the metal. Hydrogen sulphide throws down from a cold solution the sulphide (Rh_2S_3), and from a hot solution the sulphydrate ($Rh_2(SH)_6$). The insolubility of the double chloride of rhodium and sodium, ($Rh_2Cl \cdot 6NaCl$), in water, and of the double nitrate of rhodium and potassium, ($K_6Rh_6(NO_2)_{12}$), in alcohol is made use of in separating the metal from the other members of the group. Rhodium is detected in the presence of the other platinum metals by the yellow solution obtained after fusion with potassium acid sulphate and the change of color to red upon the application of hydrochloric acid.

V. RUTHENIUM. In the variety of conditions of oxidation in which they are found, the compounds of ruthenium resemble those of osmium. The lowest three oxides are basic in character, (RuO; Ru_2O_3; RuO_2), and form salts of which the three chlorides, ($RuCl_2$; Ru_2Cl_6; $RuCl_4$), are typical. The trioxide, (RuO_3), is known only in combination, where it acts as an acid and forms salts of the type $\overset{\mathrm{I}}{R}_2RuO_4$. Another oxide, ($Ru_2O_7$), known only in combination, forms salts represented by the formula $\overset{\mathrm{I}}{R}RuO_4$. The tetroxide ($RuO_4$) is volatile and similar to the corresponding oxide of osmium in its chemical behavior; it has a characteristic odor. A solution of the trichloride, (Ru_2Cl_6), throws out, when heated, a dark precipitate which is generally supposed to be an oxychloride; this precipitate is held in suspension in the liquid and gives a pronounced coloration, even in very dilute solutions. Hydrogen sulphide, acting upon solutions of ruthenium salts, precipitates a mixture of sulphides, oxysulphides, and sulphur; this mixture is brown or black, and may contain one or more of the sulphides Ru_2S_3, RuS_2, and RuS_3.

Estimation. The platinum metals are weighed in the elementary condition, obtained as described under Preparation of the various metals.

Osmium may be determined volumetrically by causing potassium iodide to act upon the tetroxide in the presence of dilute sulphuric acid, ($OsO_4 + 4KI + 2H_2SO_4 = OsO_2 + 2K_2SO_4 + 4I + 2H_2O$), and estimating by means of sodium thiosulphate the iodine thus liberated (Klobbie, Chem. Central-Blatt (1898) II, 65 (abstract). The gravimetric methods for the determination of osmium have recently been studied by Paal (Ber. Dtsch. chem. Ges. XL, 1378) and found unsatisfactory.

Separation. The separation of the platinum metals has been considered under Platinum. The following are additional references: Gibbs, Amer, Jour. Sci. [2] XXXI, 63; XXXIV, 341; XXXVII, 57; Forster, Zeitsch. anal. Chem. V, 117; Bunsen, Liebig Annal. CXLVI, 265; Chem. News XXI, 39; Deville and Debray, Compt. rend. LXXXVII, 441; Chem. News XXXVIII, 188; Wilm, Ber. Dtsch. chem. Ges, XVI, 1524; Leidie, Compt. rend. CXXXI, 888; Bull. Soc. Chim. d. Paris [3] XXVII, 179; Bannister, Analyst, XXXIX, 340; Wunder, Ztschr. anal. Chem. LII, 660, 740.

EXPERIMENTAL WORK ON THE PLATINUM METALS.

Experiment 1. *Precipitation of palladous iodide*, (PdI_2). To a solution of a palladium salt add a little potassium iodide in solution.

Experiment 2. *Precipitation of palladous sulphide*, (PdS). (*a*) Pass hydrogen sulphide through a solution of a palladous salt.

(*b*) Try the action of ammonium sulphide upon a palladous salt in solution.

Experiment 3. *Precipitation of the hydroxide or basic salt.* To a solution of a palladous salt add a little sodium hydroxide or carbonate in solution.

Experiment 4. *Precipitation of palladous cyanide.* To a solution of a palladous salt add a solution of mercuric cyanide. Try the action of potassium cyanide and ammonium hydroxide upon the precipitate.

Experiment 5. *Action of ammonium chloride upon palladous aud palladic chlorides.* (*a*) To a solution of palladous chloride add ammonium chloride.

(*b*) Saturate a solution of palladous chloride with chlorine and add ammonium chloride. The palladic salt $(PdCl_6)(NH_4)_2$ is insoluble.

Experiment 6. *Precipitation of the nitroso-β-naphthol salt*, $(Pd(C_{10}H_6NO_2)_2$.* To a solution of a palladous salt add a saturated solution of nitroso-β-naphthol in 50% acetic acid.

Experiment 7. *Precipitation of elementary palladium.* (*a*) To a solution of a palladium salt add sodium carbonate to alkaline reaction and a little formic acid, and warm. (*b*) Try the action of zinc and hydrochloric acid.†

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* Wunder, Ztschr. anal. Chem. LII, 737.

† Sulphurous acid, cuprous chloride, and ferrous sulphate will also reduce to the metal.

Experiment 8. *Precipitation of osmium sulphide,* (OsS_4). (*a*) To a solution of osmium tetroxide acidified with hydrochloric acid add a little hydrogen sulphide.

(*b*) Try the action of ammonium sulphide upon the tetroxide in solution.

Experiment 9. *Formation of potassium osmate,* (K_2OsO_4). To a solution of osmium tetroxide add a solution of potassium hydroxide. Note the yellow color.

Experiment 10. *Action of reducing agents upon osmium tetroxide.* Try the action of an alkali sulphite, formic acid, and tannic acid, respectively, upon a solution of osmium tetroxide.

Experiment 11. *Color test for osmium.* To a solution of osmium tetroxide or any other compound of osmium add a few crystals of thiourea and a few drops of hydrochloric acid, and warm. Note pink to red color. The compound is said to be ($Os(N_2H_4CS)_6Cl_3 \cdot H_2O$).

Experiment 12. *Precipitation of elementary osmium.* (*a*) To a solution of the tetroxide add stannous chloride.

(*b*) Try the action of zinc and hydrochloric acid upon a solution of the tetroxide.

Experiment 13. *Odor test for osmium.* Warm a dilute solution of osmium tetroxide, or warm with nitric acid a solution of any osmium salt of the lower condition of oxidation. Note the odor.

Experiment 14. *Precipitation of iridium sulphide,* (Ir_2S_3). Pass hydrogen sulphide through a solution of iridium tetrachloride. Note the bleaching of color preceding precipitation. Try the action of ammonium sulphide upon the precipitate.

Experiment 15. *Formation of the double chlorides of iridium with ammonium and potassium,* ($(NH_4)_2IrCl_6$ and K_2IrCl_6). To separate portions of a fairly concentrated solution of iridium tetrachloride add ammonium chloride and potassium chloride respectively.

Experiment 16. *Action of sodium hydroxide upon iridium* *tetrachloride.* To a solution of iridium tetrachloride add some sodium hydroxide in solution. Note the changes in color, dark red to green ($IrCl_3$).

$$2IrCl_4 + 2NaOH = 2IrCl_3 + NaCl + H_2O + NaOCl.$$

Warm the solution and note the change to azure blue.

Experiment 17. *Reduction of iridium salts.* (*a*) To a solution of iridium tetrachloride add oxalic acid.

(*b*) Try similarly the action of zinc upon an acid solution of the salt.

Experiment 18. *Action of ammonium hydroxide upon a rhodium salt.* Add ammonium hydroxide to a solution of a rhodium salt and allow to stand.

Experiment 19. *Precipitation of rhodium sulphide,* (Rh_2S_3). Pass hydrogen sulphide through a solution of sodium-rhodium chloride. Try the action of ammonium sulphide upon the sulphide precipitated.

Experiment 20. *Reduction of rhodium salts.* To an acid solution of a rhodium salt add zinc.

Experiment 21. *Formation of the double nitrite of potassium and rhodium,* ($K_3Rh(NO_2)_6$). To a solution of sodium-rhodium chloride add potassium nitrite in solution and warm. Try the action of hydrochloric acid upon the precipitate.

Experiment 22. *Precipitation of rhodium hydroxide,* ($Rh(OH)_3$). Note the first action and the action in excess of sodium or potassium hydroxide upon a solution of sodium-rhodium chloride. Boil the solution just obtained.

Experiment 23. *Precipitation of ruthenium sulphide,* (Ru_2S_3). (*a*) To a solution of ruthenium trichloride add hydrogen sulphide. Note the blue color preceding precipitation.

(*b*) Use ammonium sulphide as the precipitant.

Experiment 24. *Formation of the soluble double nitrite of ruthenium and potassium,* ($K_3Ru(NO_2)_6$). To a solution of ruthenium trichloride add a solution of potassium nitrite. Note the color. Add ammonium sulphide to the solution.

Experiment 25. *Precipitation of ruthenium hydroxide*, ($Ru(OH)_3$). To a solution of ruthenium trichloride add sodium or potassium hydroxide in solution.

Experiment 26. *Precipitation of metallic ruthenium*. To an acid solution of a ruthenium salt add metallic zinc.

GOLD, Au, 197.2.

Discovery. Gold is probably one of the earliest known of the metals. In very ancient records frequent mention is made of its uses. As far back as 3600 B.C. in the Egyptian code of Menes a ratio of value between gold and silver (2.5:1) is mentioned. Rock carvings of Upper Egypt dating from 2500 B.C. show crude representations of the washing of gold-bearing sands in stone basins, and of the melting of the metal in simple furnaces by means of mouth blowpipes. In fact the discovery of gold dates back to the beginnings of civilization. The search for it furnished the motive of many voyages of discovery and conquest, which resulted in the extension of civilization; and from the desire to change the base metals into gold sprang the study of alchemy, from which developed the science of chemistry.

Occurrence. Gold occurs in nature both free and in combination. Free or native gold is found (1) as vein gold, in the quartz veins which intersect metamorphic rocks, and (2) as placer gold, generally in the form of grains or nuggets, in alluvial deposits of streams. Native gold is usually alloyed with silver, which sometimes amounts to as much as fifteen per cent. of the alloy. Iron and copper are sometimes present, and bismuth, palladium, and rhodium alloys are known.

In combination gold is found as follows:

Petzite, $(AgAu)_2Te$,	contains	18–24% Au
Sylvanite, $AuAg)Te_2$,	“	26–29% “
Goldschmidtite, Au_2AgTe_6,	“	31–32% “
Krennerite, $(Au,Ag)Te_2 \cdot AuTe_2$,	“	30–34% “
Calaverite, $(Au,Ag\ Te_2 \cdot AuTe_2$,	“	38–42% “
Kalgoorlite, $HgAu_2Ag_6Te_6$,	“	20–21% “
Nagyagite, $Au_2Pb_{14}Sb_3Te_7S_{17}$,	“	5–12% “
Muthmannite, $(Au,Ag)Te$	“	22–23% “

Extraction. The six processes indicated below follow the principal methods that have been employed for the extraction of gold.

(1) *Washing or Hydraulicking.* This method is applied mainly to placer deposits. Powerful jets of water are directed upon the gold-bearing sands, causing them to pass through a series of sluices. Because of its higher specific gravity the gold is largely left behind, while the other materials are carried away.

(2) *Amalgamation (primitive).* In this process the crushed ore or the gold-bearing sand is first washed, to remove the greater part of the light, worthless material, and the remainder is rubbed with mercury in a mortar. The amalgam thus obtained is heated, whereupon the mercury is volatilized and the gold remains.

(3) *Stamp battery amalgamation.* The ore is pulverized and mixed with water, and in the form of pulp caused to pass over a series of amalgamated copper plates. Gold amalgam forms on the plates, and from time to time it is removed and cupelled.

(4) *Chlorination.* (*a*) Vat process. The crushed ore is placed loosely in large vats and moistened with water. Chlorine is forced in, and the whole is allowed to stand for about twenty-four hours. The material is then leached with water until the washings give no further test for gold. The solution of gold chloride thus obtained is treated with

sulphur dioxide, to destroy the excess of chlorine, and then with hydrogen sulphide. The gold sulphide thus precipitated is decomposed with borax and the gold is melted into bullion.

(*b*) Barrel process. Into large barrels are put water and sulphuric acid, the ore, and chloride of lime. The barrels are then closed and rotated for a period varying from one hour to four hours. At the end of that time the contents are leached and the gold is extracted as described above.

The chlorination process is generally applied to low-grade ores, and these must have been roasted unless the gold occurs in them native.

(5) *Cyanide process.* The ore, ground fine, is placed in large vats, and a dilute solution (.2–.5%) of potassium cyanide is forced in. After a time the solution is drawn off and passed over zinc shavings, upon which the gold is deposited as a black slime. The mixture of zinc and gold is either treated with sulphuric acid, to dissolve the zinc, or roasted with a flux of niter and carbonate of soda. The reactions which take place in the cyanide process may be represented as follows:

(1) $4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$

(2) $2KAu(CN)_2 + 2Zn + 2H_2O = 2KOH + H_2 + 2Zn(CN)_2 + 2Au.$

(6) *Smelting.* In smelting the gold ore is mixed with some other metallic ore appropriately chosen, and the mixture is subjected to intense heat. The gold alloys with the other metal, and the alloy is separated from the residue, or slag, and worked for gold. Three modifications of this important process are in common use, viz., lead, copper matte, and iron matte smelting. The process of lead-smelting is in outline as follows: The alloy obtained by heating a mixture of gold and lead ores is melted with zinc. The gold and silver combine with the zinc and rise

to the surface, leaving the lead below. The alloy of gold, silver, and zinc is then skimmed off and roasted. The zinc passes off, leaving the gold and silver, which are separated by electrolysis.

The Element. *A. Preparation.* As extracted from its ores gold is in the elementary condition (*vid.* Extraction).

B. Properties. Of a characteristic yellow color, gold is the most malleable and ductile of the metals. It is about as soft as silver. It is insoluble in the common acids, but is attacked by aqua regia, chlorine, bromine, and by potassium cyanide in the presence of oxygen. It is dissolved in many reactions where oxygen is set free, e.g. by selenic acid, and by phosphoric or sulphuric acid in the presence of telluric acid, nitric acid, lead or manganese dioxide, chromium trioxide, or potassium permanganate. It is not attacked when suspended in sulphuric acid and treated with oxygen gas (Lenher, Jour. Amer. Chem. Soc. XXVI, 550). It is somewhat soluble in hydrochloric acid in the presence of light and manganous chloride (Berthelot, Compt. rend. CXXXVIII, 1297), and in thiocarbamide in the presence of oxidizing agents (Moir, Proc. Chem. Soc. XXII, 105, 165). It has also been found to be slightly attacked by alkali sulphides and thiosulphates. Moissan has distilled it in the electric furnace; he finds that when alloys of copper or tin with gold are subjected to distillation, the copper and tin distil first (Compt. rend. CXLI, 853, 977). Its melting-point is 1037° C.,*—just above that of copper. Gold alloys with nearly all the metals. It is occasionally found crystallized in the cubic system. It is a good conductor of heat and electricity. Its specific gravity is 19.49.

Compounds.† *A. Typical forms.* The following compounds of gold may be considered typical forms:

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* U. S. Bureau of Standards gives 1063° C.

† For a discussion of some complex compounds see Gutbier, Ztschr. anorg. Chem. LXXXV, 353.

Oxides	Au_2O	Au_2O_2	Au_2O_3
Hydroxide			$Au(OH)_3$
Aurates			$Na_2O_2 \cdot Au_2O_2$ * $BaO_2 \cdot Au_2O_2$, etc.
Chlorides	$AuCl$	Au_2Cl_4	$AuCl_3$
Double chlorides, many of the types			$AuCl_3 \cdot \overset{I}{R}Cl$ $AuCl_3 \cdot \overset{II}{R}Cl_2$
Bromides	$AuBr$	Au_2Br_4	$AuBr_3$
Double bromides, of the type			$AuBr_3 \cdot \overset{I}{R}Br$
Iodides	AuI		AuI_3
Double iodides, of the type			$AuI_3 \cdot \overset{I}{R}I$
Sulphides	Au_2S	Au_2S_2	Au_2S_3 $2Au_2S_3 \cdot 5Ag_2S$
Double sulphides	$Au_2S \cdot Na_2S$		$2Au_2S_3 \cdot 3MoS_2$ $Au_2S_3 \cdot 3MoS_4$
Sulphites (double)	$Au_2SO_3 \cdot 3Na_2SO_3 + 3H_2O$		$Au_2(SO_3)_3 \cdot 5K_2SO_3 + 5H_2O$
Sulphates	$AuSO_4$		$Au_2(SO_4)_3 \cdot K_2SO_4$
Nitrate			$Au(NO_3)_3 \cdot HNO_3$
Cyanides	$AuCN$		$Au(CN)_3$
Double cyanides	$AuCN \cdot KCN$		$Au(CN)_3 \cdot KCN$, etc.
Sulphocyanides	$AuCNS \cdot KCNS$		$Au(CNS)_3 \cdot KCNS$

B. Characteristics. The compounds of gold are known chiefly in two conditions of oxidation, of which aurous oxide, (Au_2O), and auric oxide, (Au_2O_3), serve as types. When metallic gold is dissolved in aqua regia auric chloride is formed, a yellow crystalline salt soluble in water; when auric chloride is heated to 180° C. it goes over to aurous chloride, a white powder insoluble in water. The aurous salts resemble the salts of silver and of copper in the cuprous condition; the auric salts resemble those of aluminum and of iron in the ferric condition. The auric hydroxide, ($Au(OH)_3$), is acidic in character and unites with bases to form aurates of the type $\overset{I}{R}AuO_2$. Hydrogen sulphide precipitates brownish-black auric sulphide, (Au_2S_3 or $Au_2S_2 + S$), from cold solutions of gold salts, and steel-gray aurous sulphide, (Au_2S or Au_2S+S), from hot solutions. Salts of gold in solution are easily reduced to the metal by reducing agents.

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* See Meyer, Compt. rend. CXLV, 805.

Estimation.* *A. Gravimetric.* Gold is weighed as the metal. From solutions it is precipitated by reducing agents, such as ferrous sulphate, oxalic acid, formaldehyde, and hydrogen dioxide in alkaline solution (see also Lenher, Jour. Amer. Chem. Soc. XXXV, 546; XXXVI, 1423).

B. Volumetric. Gold may be determined volumetrically (1) by allowing potassium iodide to act upon auric chloride, ($AuCl_3+3KI=3KCl+AuI+I_2$), and estimating the iodine thus freed by means of thiosulphate (Peterson, Zeitsch. anorg. Chem. XIX, 63; Gooch and Morley, Amer. Jour. Sci. [4] VIII, 261; Maxson, Amer. Jour. Sci. [4] XVI, 155; Lenher, Jour. Amer. Chem. Soc. XXXV, 733); (2) by warming a solution of auric chloride with a measured amount of arsenious acid solution which must be in excess, ($3As_2O_3+4AuCl_3+6H_2O=3As_2O_5+12HCl+4Au$), and determining the excess of arsenious acid by iodine in the usual way (Rupp, Ber. Dtsch. chem. Ges. XXXV, 2011; Maxson, *loc. cit.*).

Separation. Gold and platinum fall into the analytical group of arsenic, antimony, and tin. From these they may be separated by the following process: fusion of the sulphides with sodium carbonate and niter, and removal of the arsenic by extraction with water; treatment of the insoluble residue with zinc and hydrochloric acid, which reduces the tin and antimony to the metallic condition; boiling with hydrochloric acid, which dissolves the tin; then with nitric and tartaric acids, which dissolves the antimony, leaving gold and platinum.

For the separation of gold from platinum and the platinum metals *vid.* Platinum.

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* See Hillebrand, Bull. 253 (1905), U. S. Geological Survey; Bahney, Bull. Am. Inst. Mining Eng. (1915), 339; Christensen, Ztschr. anal. Chem. LIV, 158; Smoot, Eng. Mining J. XCIX, 700.

From selenium and tellurium gold may be separated by oxalic acid, which precipitates the gold (A. A. Noyes, Jour. Amer. Chem. Soc. XXIX, 137).

EXPERIMENTAL WORK ON GOLD.

Experiment 1. *Extraction of gold from its ores.* (*a*) Digest for several hours in a beaker on a steam-bath about 100 grm. of finely ground gold ore with a dilute solution of potassium cyanide, adding water from time to time to replace the liquid evaporated. Filter, pass the filtrate several times through a funnel containing zinc shavings, until upon testing the liquid with a fresh piece of zinc no discoloration of the metal is observed. Dissolve the zinc in hydrochloric acid to remove the black deposit. Filter, dissolve the residue in aqua regia, remove the excess of acid by evaporation, and test for gold by stannous chloride, ferrous sulphate, etc.

(*b*) Mix in a glass-stoppered bottle about 100 grm. of finely ground "oxidized" or previously roasted ore with a little bleaching salt and enough water to give the mass the consistency of thin paste. Then add gradually enough sulphuric acid to start an evolution of chlorine. Close the bottle and shake it, to insure a thorough mixing of the contents. Allow the action to go on for several hours, agitating the mass occasionally, and taking care to have an excess of chlorine present throughout the process. Extract with water, concentrate if necessary, and test for gold in the solution. A two per cent. solution of bromine may be substituted for the materials generating chlorine.

Experiment 2. *Precipitation of the sulphide of gold,* (Au_2S_3 or Au_2S_2+S?). Into a cold solution of auric chloride pass hydrogen sulphide. Try the action of yellow ammonium sulphide upon the precipitate.

Experiment 3. *Formation of aurous iodide,* (AuI). To a solution of auric chloride add a few drops of a dilute solution of potassium iodide. Note the precipitate, and the solvent action of an excess of the reagent.

Experiment 4. *Formation of gold iminochloride and gold iminoamide, "fulminating gold,"* ($Au(NH)Cl+Au(NH)NH_2$). To a very dilute solution of gold chloride add a little ammonium hydroxide.

CAUTION. Do not attempt to isolate the precipitate. Note that neither potassium nor sodium hydroxide gives a precipitate under similar conditions of dilution, because gold hydroxide is very soluble in excess.

Experiment 5. *Formation of the "purple of Cassius."** To a very dilute solution of a gold salt add a drop or two of dilute stannous chloride solution.

Experiment 6. *Precipitation of gold.* To separate portions of a slightly acidified solution of a gold salt add solutions of ferrous sulphate, oxalic acid, and hydrazine sulphate or chloride. Try also the action of hydrogen dioxide upon an alkaline solution of a gold salt. Note the color of the precipitated gold by transmitted and reflected light.

Experiment 7. *Solvent action of certain reagents upon gold.* Try separately upon metallic gold the action of aqua regia, chlorine or bromine water, and a dilute solution of potassium cyanide.

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* Grünwald (Sprechsaal XLIII, 410) gives, as the composition of the "purple of Cassius," hydrogel of stannic acid colored by colloidal gold; *vid.* also Zsigmondy, Ann. Chem. Pharm. CCCI, 361.

CHAPTER XI.

THE RARE GASES OF THE ATMOSPHERE.

Argon, A, 39.88 Krypton, Kr, 82.92
Helium, He, 4. Neon, Ne, 20.2
Xenon, X, 130.2

Discovery. In 1892 Lord Rayleigh, while engaged in the study of the density of elementary gases, made the important observation that the nitrogen obtained from nitric acid or ammonia was about one half of one per cent. lighter than atmospheric nitrogen (Proc. Royal Soc. LV, 340). An investigation of this difference led to the discovery two years later of the gas Argon (ἀργός, *inert*) by Lord Rayleigh and Professor William Ramsay (Proc. Royal Soc. LVII, 265; Amer. Chem. Jour. XVII, 225). An experiment made by Cavendish in 1785 seems also to have resulted in the separation of this gas (Phil. Trans. Roy. Soc. (1785) LXXV, 372, and (1788) LXXVIII, 271).

In the course of analytical work on uraninite undertaken by Hillebrand in 1888, a gas which he thought to be nitrogen was obtained upon the boiling of the mineral with dilute sulphuric acid (Bull. U. S. Geol. Sur. No. 78, p. 43; Amer. Jour. Sci. [3] XL, 384). In 1895 Ramsay, whose attention had been called to Hillebrand's work, and who doubted whether nitrogen could be obtained by the method described, prepared some of the gas by Hillebrand's process from cleveite, a variety of uraninite. He then sparked the gas with oxygen over soda to remove the nitrogen. Observing very little contraction, he removed the excess of oxygen by absorption with potassium pyrogallate and examined the residual gas spectroscopically. The spectrum showed argon and hydrogen lines, and in addition a brilliant yellow line, (D_3), coincident with the helium line of the solar chromosphere discovered by Lockyer in 1868 (Proc. Royal Soc. LVIII, 65, 81). The only previous note regarding helium as a terrestrial element is a statement by Palmieri, in 1881, that a substance ejected from Vesuvius showed the line D_3 (Rend. Acc. di Napoli XX, 233); he failed to describe his treatment of the material, however, and he seems to have made no further investigation of the subject. Kayser first detected helium in the atmosphere, in 1895 (Chem. News LXXII, 89), several months after Ramsay's discovery.

The year 1898 witnessed the discovery by Ramsay and Travers of three other inert atmospheric gases. Having allowed all but one seventy-fifth of a given amount of liquid air to evaporate, and having removed the oxygen and nitrogen remaining by sparking over soda, they obtained a small amount of a gas which, while showing a feeble spectrum of argon, gave new lines as well. This newly discovered gas they named Krypton, from κρυπτός, *hidden* (Proc. Royal Soc. LXIII, 405).

By fractioning the residue after the evaporation of a large amount of liquid air they found evidence of a gas of greater density than krypton, and for this heavy gaseous element the name Xenon (ξένος, *stranger*) was chosen (Chem. News LXXVIII, 154).

The third discovery of the year by the same investigators was that of Neon (νέος, *new*), a gas of less density than argon. The first fraction obtained from the evaporation of liquid air was mixed with oxygen and sparked over soda, and the excess of oxygen was removed by phosphorus. The remaining gas yielded a new and characteristic spectrum (Proc. Royal Soc. LXIII, 437).

Occurrence.* Argon forms about one per cent. of the air by volume. It is found in small quantities in gases from certain mineral springs, e.g. Bath, Cauterets, Wildbad, Vöslau, the sulphur spring of Harrogate; in the gases occluded in rock salt, and in some volcanic gases (Moissan, Compt. rend. CXXXVIII, 936; CXXXV, 1085). It has been detected in some helium-bearing minerals, e.g. cleveite, bröggerite, uraninite, and malacon.

Helium, the existence of which was first observed in the sun, occurs in very small proportion in the terrestrial atmosphere. The chief sources of the gas have been certain rare minerals, among which are uraninite (pitch-blende), cleveite, monazite, fergusonite, samarskite, columbite, and malacon. It has been found also in some mineral springs, e.g. Bath, Cauterets, Adano, and Wildbad, and in natural and "wind" gases in amounts varying from traces to 2%. The gases yielding the largest percentages are those of southern Kansas and northern Oklahoma.

The other gases of this group are present in the air in very minute quantities. Neon is said to constitute 0.0025% and krypton 0.00002% of the atmosphere. Traces of neon have been detected in the helium from the springs of Bath.

Extraction. Argon, contaminated with a greater or less percentage of the associated gases, may be extracted by the following methods:

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* See also Ramsay, Chem. News LXXXVII, 159; Nasini, Chem. Zentr. (1904) II, 77; Pesendorfer, Chem. Ztg. XXIX, 359; Rutherford, Chem. Zentr. (1905) I, 848; Kohlschütler, Ber. Dtsch. chem. Ges. XXXVIII, 1419; Prytz, Chem. Zentr. (1905) II, 1570; Ewers, Chem. Zentr. (1906) I, 1319; Moureu, Compt. rend. CXLII, 1155; CXLIII, 795; Kitchin, Jour. Chem. Soc. LXXXIX, 1568; Czako, Ztschr. anorg. Chem. LXXXII, 249; Chem. News CVIII, 16; Collie, Jour. Chem. Soc. CIII, 419; Piutti, Atti R. Accad. dei Lincei, Roma [5] XXII, I, 140; Sieveking, Chem. Zentr. (1913) I, 58.

(1) *From atmospheric nitrogen.**—The nitrogen is passed over red-hot magnesium filings; a nitride is thus formed, while the argon is left uncombined (Ramsay). Heated lithium may be substituted for magnesium.

(2) *From air.* Induction sparks are passed through a mixture of oxygen and air contained in a vessel which is inverted over caustic potash. The oxygen and nitrogen combine and dissolve in the potassium hydroxide, leaving the argon (Rayleigh).

Helium may be obtained from its mineral sources by boiling the material with dilute sulphuric acid, or by heating *in vacuo*. From its gaseous sources it is obtained † by subjecting the gaseous mixtures to very low temperatures which cause the other gases except helium to liquefy.

Krypton and xenon are extracted as follows: After the evaporation of a large amount of liquid air the residue is freed from oxygen and nitrogen and liquefied by the immersion of the containing vessel in liquid air. The greater part of the argon can be removed as soon as the temperature rises. By repetitions of this process the three gases can be separated from one another, krypton exercising much greater vapor pressure than xenon at the temperature of boiling air (Ramsay and Travers, Proc. Royal Soc. LXVII, 330).

Neon is obtained from the gas, largely nitrogen, that first evaporates from liquid air. This gas is liquefied, and a current of air is blown through it. The material that first evaporates is passed over red-hot copper, to remove the oxygen, and after being freed from nitrogen in the usual manner, is liquefied. By fractional distillation helium and neon are removed, and argon is left behind. By the use of liquefied hydrogen helium and neon are separated, as neon is liquefied or solidified at the temperature of boiling hydrogen, while helium remains gaseous. Several fractionations are necessary to obtain pure neon (Ramsay and Travers, Proc. Royal Soc. LXVII, 330).

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* **Hamburger determines the composition of argon-nitrogen mixtures by observing the different condensation rates in liquid air (Ztschr. angew. Chem. XXVIII, I, 75).**

† **Rogers, Nat. Geog. Mag. XXXV, 441.**

Properties. The newly discovered constituents of the atmosphere are inert, colorless, probably monatomic gases, which have not been known to form definite compounds.*

Argon is somewhat soluble † in water. Its density is 19.96 and its specific heat 1.645. It solidifies at −191° C., melts at −189.5° C., and boils at −185° C. It has been condensed to a colorless liquid (Baly and Donnan, Jour. Chem. Soc. (London) LXXXI, 914). Argon gives two distinct spectra, according to the strength of the induction current employed and the degree of exhaustion in the tube. When the pressure of the argon is 3 mm. the discharge is orange-red and the spectrum shows two particularly prominent red lines.‡ If the pressure is further reduced, and a Leyden jar is intercalated in the circuit, the discharge becomes steel-blue and the spectrum shows a different set of lines (Crookes, Amer. Chem. Jour. XVII, 251).

Helium is slightly soluble § in water. Its density is 1.98, and it boils at about −268.5° C. It was liquefied by Onnes (Proc. k. Akad. Wetensch. Amsterdam XI, 168; XIII, 1093) and its density in liquid form was found to be 0.122. Its spectrum || is characterized by five brilliant lines,—one each in the red, yellow, blue-green, blue, and violet. Reference has already been made to the yellow line D_3.

Krypton is less volatile than argon. Its density is 41.5. Its melting-point is given as −169° C., and its boiling-point as −152° C.¶ Its spectrum** is characterized by a bright line in the yellow and one in the green.

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* Fisher and Schröter, Ber. Dtsch. chem. Ges. XLIII, 1435, 1442, 1454, 1465.

† 100 volumes of water will dissolve 3.7 volumes of argon at 20° C.

‡ Paulson, Physik XV, 831.

§ 100 volumes of water will dissolve about 1.4 volumes of helium at 20° C.

|| Curtis, Proc. Royal Soc. LXXXIX, 146.

¶ Erdmann, Chem. Ztg. XXXI, 1075.

** See Baly, Proc. Royal Soc. LXXII, 84.

Xenon also is less volatile than argon, and it has a much higher boiling-point. Its density is 65.35. Its melting-point is said to be −140° C., and its boiling-point −109° C.* Its spectrum † is similar in character to that of argon, though the position of the lines is different. With the ordinary discharge the glow in the tube is blue and the spectrum shows three red and about five brilliant blue lines. With the jar and spark-gap the glow changes to green and the spectrum is characterized by four green lines (Ramsay and Travers, Chem. News LXXVIII, 155).

Neon is more volatile than argon. Its density is 10.1. Its melting-point is given as −253° C., and its boiling-point as −243° C.‡ Its spectrum § is characterized by bright lines in the red, orange, and yellow, and faint lines in the blue and violet.

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* Erdmann, Chem. Ztg. XXXI, 1075.

† See Baly, Proc. Royal Soc. LXXII, 84.

‡ Erdmann, *loc. cit.;* Dewar, Proc. Royal Soc. LXVIII, 360.

§ See Baly, *loc. cit.;* Merton, ibid. LXXXIX, 447.

CHAPTER XII.

SOME TECHNICAL APPLICATIONS OF THE RARER ELEMENTS.*

Lithium has found some use in the preparation of artificial mineral waters and in medicine. It has also been used in fireworks and signal rockets (U. S. Press Bull. May, 1918).

Beryllium compounds are said to have been employed in the manufacture of mantles for incandescent gas lighting (Baskerville, Eng. and Min. Jour. LXXXVI, 907).

The use of radium in medicine is well known. Its employment in the manufacture of luminous paints has developed greatly during the war. Mesothorium is also being used in luminous paints. (Met. Chem. Eng. XVII, 357; Eng. and Min. Jour. (1918) 1124).

The chlorides of the rare earths† have been subjected to electrolysis (Muthmann and Weiss, Liebig, Ann. CCCXXXI, 1; CCCXXXVII, 370), and have yielded a so-called "mischmetal" (45% Ce, 35% La, Pr, Nd, and 20% Sm, Er, Gd, Y), with which, as with aluminum in the Goldschmidt process, it has been found possible to reduce a number of the oxides (e.g. MoO_3, V_2O_5, Nb_2O_5, and Ta_2O_5) to the elementary condition. The oxides of cerium, neodymium, praseodymium, and erbium seem to promise some application in the coloring of porcelain and glass (Waegner, Chem. Ind. (1904) XXVII, No. 12). Cerium salts have been used, like aluminum salts, as mordants in dyeing (Witt, Chem. Ind.

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* In Mineral Foote-Notes published bi-monthly by the Foote Mineral Co. of Philadelphia, Penn., the author of this book has reviews of the most recent technical literature upon the rarer elements.

† A good summary of the technological uses of the rare earths thorium and zirconium may be found in Levy, The Rare Earths, Chapter XXI (Longmans, Green and Company), and Johnstone, The Rare Earth Industry (Lockwood, London).

XIX, 156), and Barbieri (Atti R. Accad. Lincei, Roma [5] XVI [1], 395) has described their uses as catalyzing agents, their behavior being similar to that of manganese compounds. Ceric sulphate has been used in photography to reduce the density of negatives (Lumière frères and Seywetz, Chem. Ztg. Repert. (1900), 80), and both ceric nitrate and ceric sulphate have been used in making photographic paper (Lumière, Compt. rend. (1893) CXVI, 574; Chem. Ztg. Repert. (1892), 180, 235). Cerium oxalate, cerium hypophosphate, and cerium-ammonium citrate have found uses in medicine for sea-sickness and nervous disorders. The nitrates and salicylates of the rare-earth elements are used as antiseptic agents (Merck's Ber. (1897), 39; Kopp, Therap. Monatshefte (1901), Feb. No. 2). For purposes of oxidation ceric sulphate has been found to be a fair substitute for well-known oxidizing agents such as potassium permanganate (Zeitsch. f. Electrochem. IX, 534; Chem. Ztg. XXIX, 669). Salts of yttrium, lanthanum, erbium, and ytterbium have been used in disinfecting and in embalming. Praseodymium hydroxide and the acetates of praseodymium, neodymium, and lanthanum have been employed as mordants, as have also mixtures of the sulphates of these earths (Baskerville and Foust). The use of the peroxides of the cerium earths in making rust-proof colors has been suggested. Cerium compounds are finding extensive use in the manufacture of arc-lamp electrodes (English Patents 414,707 (1910); 21,374 and 8,150 (1909)).

Oxygen compounds of the rare earths have been employed as catalytic agents in the sulphuric acid contact process, and some of the chlorides have been used as contact material in decomposing heated hydrochloric acid gas. Cerous-ceric sulphate has found use in the manufacture of electric batteries (Baskerville, Paper on the Uses of the Rare Earths). The employment of cerium alloys, pyrophoric bodies,* in

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* Kellerman, Die Ceritmetalle und ihre pyrophoren Legierungen, pub. by W. Knapp, Halle (1912).

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gas and cigar lighters is fairly familiar (Böhm, Chem. Ztg. XXXIV, 361; Dederichs, Pharm. Post, XLVI, 397).

The use of thorium nitrate in the manufacture of mantles for incandescent gas lights is a well-known application of thorium, and the development of this growing and important industry has been largely responsible for the advances in rare-earth chemistry. The mantles contain about 99% of thoria and about 1% of ceria (Welsbach Co. Bulletins (1907–8)).

Thorium carbide is said to have been used in filaments for incandescent electric lamps, and the oxide in electric glowers such as the Nernst lamp. Yttria and zirconia are better for the latter purpose because they are less volatile. Bolton (Zeitsch. f. Electrochem. XVII, 816) states that water which has been in contact with thorium seems to prolong the life of certain animal organisms, while the action upon vegetable life is injurious.

Zirconium has found application in the manufacture of the Nernst glowers, about 85% of zirconium oxide to 15% yttrium-earth oxides of the higher atomic weights being used in their manufacture. The carbide of zirconium is said to be an excellent conductor of electricity; ninety parts of it mixed with ten parts of the metal ruthenium have been made into filaments for use in the zirconium lamp (Sander, Jour. f. Gasbel. XLV II, 203, or Chem. Zentr. (1905) I, 1290; Böhm, Chem. Ztg. XXXI, 985, 1014, 1037, 1049). The use of zirconium nitrate as a food preservative has been mentioned (Baskerville, Eng. and Min. Jour. LXXXVII, 548). Ferro-zirconium is finding some use as a scavenger and hardening agent in steel manufacture.

Zirconium oxide has been used as an enamel (Jost, German Patent 285,981 (1914); Leuch, 285,344 (1914); and refractory vessels which will stand a temperature of 2000° C. have been made from oxides of zirconium and thorium (Knöfler, German Patent 285,934 (1913); Arnold, U. S. Patents 1,121,889 (1914), 1,157,662 (1915); Weiss and Lehman, Ztschr. anorg. Chem. LXV, 218). Zirconia is the principal constituent of zirkite, a commercial product designed to withstand the heat of high temperature furnaces (Meyer, Mineral Foote-Notes, Philadelphia, Mar.–Apr. 1919.)

Thallium has been used in the manufacture of optical glass, and is said to give a higher refractive power than lead (Lenher, Electrochem. Ind. (1904), 11, 61). Certain compounds of thallium are being employed to prolong the life of the tungsten filament in incandescent lamps.

For titanium a number of applications * in the arts have been found. As ferro-titanium, an alloy containing from 30% to 55% of titanium, it is used in the manufacture of steels; it is said to add greatly to their tensile strength and elastic limit. Titanium-steel rails† have given excellent service at the throat of the New York Central R. R. terminal yard in New York City, showing practically no wear in one year where the life of a rail had been from six to eight months. Titanium improves iron and steel by uniting, in the course of manufacture, with the oxygen and nitrogen, which pass off in slag; the formation of blow-holes is thus prevented. Cuprotitanium is employed in the manufacture of brass. The metal has been used to a certain extent as a filament for incandescent electric lamps. Rutile, titaniferous magnetite, titanium carbide, and titanium suboxide are all finding use as electrodes with carbon blocks in arc lamps. Electrodes containing titanium give better distribution of color and light, higher efficiency, and lower cost of maintenance. The electrodes made of the carbide and of the sub-oxide are generally used as anodes. Other commercial uses of titanium are found in the employment of rutile for giving a yellow color to porcelain tile and to artificial teeth; of titanium chloride and titanous sulphate as mordants; and of titanous potassium oxalate as a mordant and yellow dye in the treatment of leather. Titanic oxide

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* See Levy, Chapter XXII, foot-note, page 196.

† See Dudley, Use of Titanium in Bessemer Rails, Jour. Ind. and Eng. Chem. II, 299.

has been used as a protective paint for iron and steel, and to a limited extent as an incandescent medium for gas lights. The ferrocyanide has found employment as a substitute for Schweinfurth's green (Baskerville, Eng. and Min. Jour. LXXXVII, 10). On combustion titanium gives a brilliant light, a characteristic that has led to its use in pyrotechnics. The nitride has been suggested as a source of nitrogen for fertilizers, for the element combines readily with nitrogen, and yields ammonia on being heated with hydrogen.

Vanadium has found employment in a photographic developer, in a fertilizer for plants, in coloring material for glass, and with anilin in a black dye. Vanadyl phosphate has been found to behave physiologically like potassium permanganate (Ephraim, Das Vanadin und seine Verbindungen, 83). Vanadic acid (V_2O_5) is employed in making a waterproof black ink with tannic acid, in manufacturing sulphuric acid by the contact process (Kuster, Chem. Zentr. (1905) I, 328), as a substitute for gold bronze, and as a catalyzer to accelerate oxidation processes, such as the oxidation of sugar to oxalic acid, of alcohol to aldehyde, and of stannous to stannic salts (Naumann, J. pr. Chem. (2) LXXV, 146). Some of the oxides have been used in ceramic decoration, and the trioxide and chloride as mordants (Baskerville, Eng. and Min. Jour. LXXXVII, 518). Probably of more importance than any of the foregoing uses of vanadium is its employment in the manufacture of steel, which gains greatly in elasticity and tensile strength by the presence of from .15% to .35% of this element, introduced as ferro-vanadium, an alloy containing about 30% of vanadium. (See pamphlets by J. Kent Smith, Amer. Vanadium Co.)

The use of the tantalum filament as a substitute for carbon was an interesting step in the development of incandescent electric lighting. The tantalum lamp produces a light of one candle-power for every two watts of electrical power, as against three and one-tenth watts required by the ordinary carbon lamp. The tantalum filament, however, has now been superseded to a great extent by tungsten. (Mineral Resources U. S. 1908–1910.) The hardness of tantalum and its resistance to chemical action have suggested its use in pens; and pure or alloyed with iron, silicon, boron, aluminum, tin, titanium, or nickel, it has been used in watch springs, clock movements, anvils, and tools for cutting (Baskerville, Eng. and Min. Jour. LXXXVI, 1100; Siemens, German Patent 282,575 (1913)). An alloy with gold and copper is recommended for many purposes as a substitute for gold (Siemens, German Patent 284,241 (1913)). Tantalum has found some use as a cathode in electrolysis, being substituted for platinum (Brunck, Chem. Ztg. XXXVIII, 565), and as an electrical resistance wire by coating it with platinum to prevent oxidation at high temperatures (Simpson, U. S. Patent 1,175, 693 (1916)). It has been employed in the manufacture of burnishers for use in dentistry.

The element niobium is said to have found some use in the manufacture of filaments for incandescent lamps, and some of its compounds in the preparation of mantles for gas lighting (Baskerville, Eng. and Min. Jour. LXXXVI, 960).

Molybdenum alloyed with iron has been used in the manufacture of steel (Mineral Resources U. S. 1914). Molybdenum wire is said to have found some use as a support for tungsten filaments (Mineral Resources U. S. 1908–1914). Ammonium molybdate is an important reagent in the analysis of phosphates. It has also been applied in fire-proofing and as a germicide and disinfectant. Sodium molybdate is employed in coloring pottery and porcelain, and in dyeing silks and woolens. Molybdenum tannate with logwood extracts finds use in dyeing leather, and "molybdenum indigo" (Mo_2O_7) is a useful but expensive pigment for india rubber (Baskerville, Eng. and Min. Jour. LXXXVI, 1055).

Doubtless the most interesting use of tungsten at present is that of its metallic filament in electric lighting.* With its melting-point of about 3000° C., this metal makes a lamp which gives one candle-power of light for every one and twenty-five hundredths watts of electrical power, as against two watts required by the tantalum lamp; and which has a life of one thousand or more hours, or about twice as long as that of the carbon and tantalum lamps. A disadvantage of the tungsten lamp, at first, was the extreme fragility of the filament. Recent improvements in manufacture, however, have made feasible not only the safe shipment of tungsten lamps, but the equipment of railroad trains and automobiles with them. Siemens and Halske, A.-G., of Berlin, Germany, have taken out patents on a process for increasing the ductility of tungsten by adding 8%–20% of nickel.† The high melting-point of the element has suggested its possible use in the manufacture of crucibles (Mineral Resources U. S. 1908–1914). Certain salts are used in weighting silks. Sodium tungstate is employed in fireproofing draperies, as a mordant in dyeing, and with potassium tungstate in the production of magenta and saffron bronzes. Tungstic oxide is used as an oil and water color (Baskerville, Eng. and Min. Jour. LXXXVII, 203). Calcium tungstate, on account of its fluorescence, is used in the Roentgen ray apparatus; lead tungstate has been substituted for white lead in paints. Compounds of tungsten have been employed in coloring glass and porcelain. The alloy with aluminum is used in French automobile construction, and the alloy with aluminum and copper in the blades of propellers. Alloyed in small percentages with steel, tungsten is used for the following purposes: (*a*) to toughen armor plate; (*b*) to stiffen car springs; (*c*) to increase the permanency of magnets; (*d*) to increase the vibratory response in sounding-plates and wires for musical instruments; (*e*) to prevent projectiles and high-speed tools from losing their temper when hot (Van Wegenen, Chem. Engineer IV, 217). Hale (Eng. and Min. Jour. LXXXVII, 813) states that tungsten steel is poor shock-resisting steel, but has great crushing strength. Tungsten has recently found many other technical applications, e.g. standard weights, acid-proof dishes and tubes, pens, and knife blades (Mineral Resources U. S. 1914; Fink, J. Ind. Eng. Chem. v, 8; Mineral Industry, (1914) 759, 1915).

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* For a full discussion of tungsten, tantalum, osmium, and zirconium filaments in electric lighting, see Weber, Die elektrischen Metallfadenglühlampen, pub. by M. Jänecke, Leipzig.

† For a discussion of methods of preparing wire, see Müller, Ztschr. angew. Chem. XXVI, 422.

Uranium salts are used in the production of certain velvety-black glazes for pottery, and of greenish-yellow iridescent glass. Uranium increases the strength of cast iron or semi-steel (Iron Age, C 1413, CI 77). Mixed with calcium fluoride, in arc lamps it gives an intense snow-white light of high photographing power (Elect. World LXX, 1002). The employment of the carbide in filaments for electric lighting has also been mentioned (Baskerville, Eng. and Min. Jour. LXXXVII, 257). Uranium acetate has been used in medicine as a precipitant of proteids.

Elementary selenium has the peculiar property of being a fairly good conductor of electricity in the light,* while in the dark it is practically a non-conductor. This property has been made of service in the construction of electrical apparatus for automatically lighting and extinguishing gas-buoys, for exploding torpedoes by a ray of light, for telephoning along a ray of light, for transmitting sounds and photographs to a distance by telegraph or telephone wire, and for measuring the quantity of Roentgen rays in therapeutic applications (Hess, Mineral Resources U.S. 1906–1914). Selenium cells have been constructed for measuring the intensity of light (Huels, Bull. Univ. Wisconsin, Madison, No. 157, 419). Selenium compounds are finding important applications in the manufacture of red enamel ware, in the enameling of steel, and in the production of red glass for use in railroad signals (Jour. Ind. and Eng. Chem. IV, 539; Fenaroli, Chem. Ztg. XXXVIII, 177, 873). The selenides and organic compounds of selenium have been suggested for use in making dyes (Wasserman, German Patent 286,950 (1913); Bauer, Ber. Dtsch. chem. Ges. XLVII, 1873). Sodium selenite has been employed to show the reducing power of bacteria (Merck's Index, 1907). Selenium has found some use in the vulcanization of rubber (Jour. Ind. and Eng. Chem. X, 117).

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* Ries (Physikal. Ztschr. XII, 480) discusses reasons for this property.

Tellurium has shown certain peculiar behavior toward electricity which would indicate that some electrical uses may be found for the element (Hess, Mineral Resources U. S. (1908), 719). The tellurides have been mentioned as of possible value in making dyes, as well as in coloring glass (Wasserman, *loc. cit.,* Fenaroli, *loc. cit.*). Tellurium is said to have some use in forming high-resistant alloys, and in medicine as an antisudorific agent.

The element platinum is finding increasing use in jewelry, and continues to be important in the manufacture of chemical apparatus. Recently 2000 kilos were reported as having been used in one year in the production of pins for artificial teeth. Its application in the sulphuric acid contact process is most important. The use of platinum in electrical industries is gradually becoming less, on account of the substitution of nickel-chromium alloys, molybdenum, and tungsten (Mineral Resources U. S. (1914), 338).

Iridium, alloyed with osmium, is employed for compass-bearings and for tips of gold pens. Its alloy with platinum is used in the manufacture of laboratory apparatus and for standard weights and measures. The black oxide finds use in china-painting.

Osmium has long been employed as a stain in microscopic work,* and more recently as a filament for incandescent lamps (Jour. f. Gasbel. XLIV, 101; XLVIII, 184; Chem. Zentr. (1907) II, 433).

Palladium, because of its hardness and unalterability in air, is used for graduated surfaces of fine apparatus. It has also found use in alloys for dental work, and on account of its comparatively low fusing-point it is employed in soldering the other platinum metals.

Rhodium alloyed with platinum (10% of Rh) has been used in making thermo-elements for high-temperature work.

Ruthenium, as has been already stated, has been mixed with zirconium carbide for use in the filament of the zirconium lamp.

The uses of gold in coinage, in jewelry, and in dentistry need no description.

An interesting application of helium was worked out in connection with recent war activities, viz.: its use in ballooning (Eng. and Min. Jour. Feb. 8, 1919, p. 273). This gas has about 92% of the buoyant effect of hydrogen and is non-inflammable. A cheap process for its extraction from natural gas has brought down the estimated cost from $1700 to 10 cents a cubic foot. At the close of hostilities 147,000 cubic feet of nearly pure helium stood ready for shipment.

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* Schultze, Zeitsch. f. wiss. Microskop. XXVII, 465.

CHAPTER XIII.

THE QUALITATIVE SEPARATION OF THE RARER ELEMENTS.

The following schemes of separation will give some idea of the problems of qualitative analysis in the presence of some of the rarer elements. None of the schemes given considers the possible presence of all of these elements.

Tables I and III include original methods which have given fairly satisfactory results in the hands of the author's classes.

Tables II, VI, and VIII, together with a considerable part of the material contained in the accompanying directions and notes were prepared from the publications of A. A. Noyes and his associates, to whom the author acknowledges his indebtedness. No attempt has been made here to take up the study of the separation methods in detail, nor to indicate the processes used for the separation of the commoner elements from one another when the rarer elements are not involved. All these processes are fully discussed in the original papers, to which reference is made.

Tables IV and V offer processes worked out by James, but rather beyond the scope of any but advanced students. They have been added, however, without explanatory notes, merely to show the best methods of attack on the complicated problem of rare earth analysis; and references to the original papers have been furnished.

In Table VII the method suggested by Böhm has been put into diagrammatic form. In this scheme no attempt was made by Böhm to give anything further than a process for the separation of the more important rare earths from other elements and from one another. To make the table more complete, however, methods for the separation of the other rare elements mentioned have been supplied.

I

THE ALKALI GROUP.

Before taking up the analysis as outlined in Table I, the student is advised to review by means of the following experiments the reactions of the elements involved, and to put the results into tabular form. Use solutions of the chlorides of Li, Na, K, Rb, and Cs, respectively. Perform the experiments upon separate portions of these solutions. (1) Addition of solution of H_2PtCl_6; (2) of $Na_3Co(NO_2)_6$; (3) evaporation with $Al_2(SO_4)_3+H_2SO_4$; (4) dehydration of chlorides with amyl alcohol; (5) review of flame and spectroscopic tests.

THE QUALITATIVE SEPARATION.

TABLE I.

The alkalies present as chlorides.*

Dissolve about 1–5 grms. of the mixed salts in water, and dehydrate with amyl alcohol.

R	F
Na, K, Rb, Cs. Dissolve in a few drops of water, add H_2PtCl_6.	Li. Confirm by spectroscope.

P	F
CsRb(K) as chloroplatinates. (1) Test a portion of the precipitate on a platinum wire before the spectroscope. (2) Decompose by gentle ignition, add a few drops of water and filter, add a little solid aluminum sulphate, dissolve and crystallize. $CsAl(SO_4)_2 \cdot 12H_2O$ crystallizes before $RbAlSO_4 \cdot 12H_2O$. See page 12.	K,Na. Add an equal volume of alcohol. Filter, and wash with water and alcohol (1–1).

P	F
K. Confirm by spectroscope.	Na. Add a few drops of a one-per cent. solution of H_2SO_4 in alcohol. Ppt. Na_2SO_4. If no precipitate forms saturate with HCl gas. Ppt. NaCl.

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* If the alkalies are present as salts of mixed volatile acids, they may be converted to the sulphates by evaporation with H_2SO_4 to the fuming-point. The sulphates may be converted to the carbonates by treating with an excess of $Ba(OH)_2$ in solid form, filtering off the $BaSO_4$ and insoluble excess of $Ba(OH)_2$, and removing the $Ba(OH)_2$ in solution as insoluble $BaCO_3$ by passing CO_2 and boiling. The alkalies are left in solution as carbonates, from which form they may easily be converted to any salt desired.

II

THE ALUMINUM AND IRON GROUP.

Before beginning work upon this analysis the student should review the reactions of the elements involved. The common elements Fe and Al are included in the experiments suggested, as they are typical members of their respective subdivisions.

Upon separate solutions of the following salts: $FeCl_3$, $TiCl_4$, $TlCl_3$, $ZrCl_4$, $AlCl_3$, $BeCl_2$, UO_2Cl_2 and $NaVO_3$ perform the following experiments, and record the results in tabular form: (1) Add $HCl+H_2S$; (2) add $NH_4OH+(NH_4)_2S$ to the product of (1); (3) add $NaOH+Na_2O_2$ to an HCl solution of any precipitate obtained in (2); (4) add NH_4OH to portions of the original solutions; (5) warm solutions of the Al, V, Be, and U salts in a closed bottle with $NaHCO_3$; (6) shake separate portions of HCl(1.12) solutions of the hydroxides of $\overset{III}{Fe}$, Ti, Zr and $\overset{III}{Tl}$ with ether in a separation funnel, and test the resulting layers; (7) dehydrate the chlorides of $\overset{III}{Fe}$, Ti, Zr and $\overset{III}{Tl}$ with amyl alcohol; (8) add $NaHPO_4$ to solutions of Ti and Zr salts in presence and absence of H_2O_2; (9) add Na_2SO_3 followed by KI to solutions of $\overset{III}{Tl}$ and $\overset{III}{Fe}$ salts; (10) add strong HCl to concentrated solutions of chlorides of Be and Al; (11) dehydrate concentrated solutions of the nitrates of Be and Al with amyl alcohol; (12) add $NaHPO_4$ to solutions of U and V salts.

DIRECTIONS AND NOTES FOR Al AND Fe GROUP.

Boil out H_2S if present. Add NH_4OH in distinct but not large excess; note precipitate; pass H_2S to saturation, warm, filter, wash with dilute $(NH_4)_2S$ and then with water. Avoid the use of $(NH_4)_2S$ as precipitant because of its solvent action upon Ni. Transfer the precipitate with 5–20 $\overline{\text{cm.}}^3$ of HCl (1.12). Stir before warming, then boil a few minutes. If a black residue remains add a few drops of HNO_3

(1.42) and boil. Evaporate nearly to dryness with HNO_3 to remove HCl. Dilute to 10–20 $\overline{\text{cm.}}^3$,* make alkaline with NaOH, add water to double the volume of the liquid. Add gradually 0.5–3 grms. of Na_2O_2 with stirring. Add 5 $\overline{\text{cm.}}^3$ of 10% Na_2CO_3, unless it is known that the alkali earths are absent; boil to remove excess of Na_2O_2. Cool, add equal volume of water, and filter.

HCl is added before HNO_3 to avoid oxidizing effect of HNO_3 and formation of H_2SO_4, which in turn interferes with test for CrO_4 by Ba and Pb salts. HNO_3 is necessary to dissolve sulphides of Ni, Co, and V. HCl must be removed by evaporation, because chlorides interfere with test for CrO_4 by Pb. If $(NH_4)_2S$ precipitate is allowed to stand for some time before treating it with acid, or if the mixture is heated a long time after precipitation, $ZrO(OH)_2$ and $TiO(OH)_2$ tend to remain undissolved after treatment with acids, because of partial dehydration. These compounds may be dissolved by HF in Pt dish, and HF removed by evaporation with HNO_3 or HCl. Na_2O_2 oxidizes Fe, Mn, Co, Ni, $\overset{\text{I}}{\text{Tl}}$, Cr, and U. U goes into solution as peruranate.

Al Group.—To the filtrate from the Na_2O_2 precipitate add HNO_3 (1.20), keeping the solution cool until it reacts faintly acid. Dilute the solution to 100 $\overline{\text{cm.}}^3$; transfer to a flask, and place a funnel in the mouth of the flask. Add $NaHCO_3$ until the mixture, on shaking, no longer turns litmus red at once, and add about 1–5 grms. of solid $NaHCO_3$. Warm 20–30 minutes on a water bath. Cool and filter.

Alkaline solution is kept cool during neutralization to avoid reduction of $\overset{\text{VI}}{\text{Cr}}$ to $\overset{\text{III}}{\text{Cr}}$ salt. Care must be taken to keep strictly to the directions about the use of $NaHCO_3$. Stronger solutions dissolve Be.

Dissolve the precipitate in dilute HCl and add NH_4OH in moderate excess. Heat to boiling, filter, and wash thoroughly. Dissolve the precipitate in dilute HNO_3, evaporate to a few $\overline{\text{cm.}}^3$, and dehydrate with amyl alcohol. Be dissolves. To the filtrate from the $NaHCO_3$ treatment add HNO_3 (1.20) until the solution is distinctly acid but not in excess. If the solution is colorless, Cr is absent, and the treatment with Pb salt and H_2S may be omitted. If Cr is absent neutralize the acid with NH_4OH, add acetic acid, 1–2 grms. of $(NH_4)_2SO_4$, 2 grms. of Na_2HPO_4, and heat to boiling. Filter, and wash with a solution of $(NH_4)_2SO_4$. Dissolve in dilute HCl, evaporate, add NaCl and $K_4FeC_6N_6$. Dark red = U.

---

* If rare earths are to be tested for, treat this solution, only faintly acid with HNO_3, with NaF to complete precipitation of fluorides of rare earths Filter and reserve precipitate for rare earth analysis. Continue with filtrate as directed above.

Neutralize the filtrate from the $NaHPO_4$ filtrate with NH_4OH in slight excess and saturate with H_2S. Pink or violet = V.

Fe Group.—Dissolve the Na_2O_2 precipitate in 5–30 $\overline{cm.}^3$ of dilute HCl, warm, filter off paper, etc., and evaporate to about 2 $\overline{cm.}^3$ Add about 5 $\overline{cm.}^3$ of strong HNO_3; and boil to remove HCl. Add 5–20 $\overline{cm.}^3$ of strong HNO_3 and boil, adding 0.5 grm. of $KClO_3$. Filter off the MnO_2 on glass wool or asbestos.

HCl is used rather than HNO_3 because HNO_3 does not dissolve MnO_2 readily. HCl is removed by HNO_3 because HCl dissolves MnO_2.

If phosphates are absent (if present use acetate method) add NH_4OH in distinct excess to the filtrate from the MnO_2, filter, wash, and remove the water present, by suction if necessary. Dissolve in HCl (1.12), being careful to use this strength of acid. Add to the cold solution an equal volume of ether, and shake in a separation funnel. Draw off the layers, and repeat this operation with the water layer until the ether layer remains colorless.

The extraction of $FeCl_3$ is most complete when the acid is 1.12. The absence of $FeCl_3$ from the ether layer may be shown by lack of color. The water layer may have yellow color due to TiO_3. Phosphoric acid does not interfere with the separation.

Evaporate the ether extract on a water or steam bath, dissolve the residue in a little dilute H_2SO_4 and water. To the cold solution add a little KI solution and Na_2SO_3 until iodine color has disappeared. Yellow TlI indicates Tl. Confirm by green flame. Evaporate the water layer on a steam bath until the ether is expelled. Add dilute H_2SO_4 and evaporate to the fuming-point. Cool, add 5 $\overline{cm.}^3$ of water, 10 $\overline{cm.}^3$ of 3% H_2O_2, and 10 $\overline{cm.}^3$ of 10% Na_2HPO_4 solution. Orange-red coloration = Ti; white, flocky precipitate, $ZrOHPO_4$ = Zr. Allow the mixture to stand about an hour before filtering. If filtrate is still colored, add powdered Na_2SO_3 until the color bleaches. Precipitate, white, flocky $TiOHPO_4$ = Ti.

The precipitation of the phosphate of Zr is slow, so that some time should be allowed for it to form. The oxidation with H_2O_2 is necessary to keep the Ti from precipitating with the Zr. If rare earths are present they should be removed by HF before testing for Ti and Zr.

TABLE II.*

To a solution containing members of this group add NH_4OH and pass H_2S.

- P: Al, Cr, Be, Ti, Zr, V (partly), as hydroxides. Fe, Zn, Co, Ni, Mn, U, Tl, as sulphides. Dissolve in $HCl+HNO_3$, evaporate, add NaOH, Na_2O_2, and Na_2CO_3.
  - P: (Fe Group.) **Mn, Fe, Co, Ni, Tl, Ti, Zr, Zn (partly), as hydroxides.** Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$.
    - P: **Mn**
    - F†: Add NH_4OH
      - P: Fe, Ti, Zr, Tl, as hydroxides.‡ Dissolve in HCl (1.12) and shake with ether.
        - **Ether layer.** Evaporate, dissolve in dilute H_2SO_4, add KI and Na_2SO_3.
          - P: **TlI Yellow.**
          - F: **Fe**
        - Water layer. Add H_2SO_4, evaporate, add H_2O_2 and Na_2HPO_4.
          - P: **Zr(OH)PO$_4$**
          - F: Yellow TiO_3. Add Na_2SO_3. P·Ti(OH)PO$_4$.
      - F: **Co, Ni, Zn**
  - F: (Al Group.) Zn, Cr, Al, V, Be, U, in solution as sodium salts. **Add** HNO_3, dilute, add $NaHCO_3$, and heat in a closed bottle.
    - P: Zn, Al, Be, as hydroxides or carbonates. Dissolve in HCl, add NH_4OH.
      - P: Be, Al, as hydroxides.§ Dissolve in HCl, add ether, and saturate with HCl (gas).
        - P: **Al**
        - F: **Be**
      - F: **Zn**
    - F: Add HNO_3 to neutrality, and add $Pb(NO_3)_2$.
      - P: $PbCrO_4$
      - F: Pass H_2S.
        - P: **PbS**
        - F: Add bromine, boil, neutralize, add $HC_2H_3O_2$ and Na_2HPO_4.
          - P: $UO_2NH_4PO_4$. Dissolve in HCl, add $NaCl+K_4Fe(CN)_6$. P red brown $(UO_2)_2FeC_6N_6$.
          - F: Add NH_4OH and saturate with H_2S. Red solution indicates **V.**
- F: Alkalies and alkali earths (in the absence of phosphoric acid).

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* Before using this table the student should carefully study the original article (Noyes, Bray and Spear, Jour. Amer. Chem. Soc. xxx, 481).

† Test for H_3PO_4 and if present modify the treatment.

‡ A modification of this treatment will be found on next page.

§ A satisfactory qualitative separation of Be and Al may be accomplished by dehydrating the nitrates with amyl alcohol. The $Be(NO_3)_2$ dissolves. (Browning and Kuzirian).

A modification of the method described in Table II as applied to the separation and detection of iron, thallium, zirconium, and titanium, starting with the hydroxides.*

Dissolve hydroxides in the least possible amount of H_2SO_4. Treat with H_2O_2, a red coloration indicating titanium. Treat with Na_2HPO_4 in the presence of NaOH† and add H_2SO_4 to acidity.

P
$ZrOHPO_4$

F
Treat with NaOH.

P
Fe } as hydroxides
Tl } or phosphates.
Dissolve in H_2SO_4. Treat with
Na_2SO_3+KI and filter.

F
Treat with H_2SO_4, Na_2SO_3 and
Na_2HPO_4, and filter.

P
$TiOHPO_4$

P
TlI

F
Boil to remove SO_2, add H_2O_2 to break
up iodide, boil to remove iodine, add
KSCN. Red coloration indicates Fe.

---

* Browning, Simpson, and Porter, Am. Jour. Sci. XLII, 106.

† This step is to prevent the excess of acid when sodium phosphate is added acidity interfering with the ready precipitation of zirconium phosphate. Gentle warming after the addition of sodium hydroxide gives good results, but in no case should the solution be boiled, and if warmed it should be cooled and treated with hydrogen dioxide before acidifying with sulphuric acid.

III

THE RARE EARTH GROUP.

Before taking up the analysis indicated in Table III the student is directed to review the reactions of the elements involved, and to put the results in tabular form.

Upon separate solutions of the following salts, $Y(NO_3)_3$, $Ce(NO_3)_3$, $Pr(NO_3)_3$, $Nd(NO_3)_3$, $La(NO_3)_3$, $Ce(NO_3)_4$ and $Th(NO_3)_4$, try the action of the following reagents in solution: (1) NaOH, NH_4OH, or KOH: (2) Na_2CO_3 or K_2CO_3; (3) $(NH_4)_2CO_3$; (4) $H_2C_2O_4$; (5) $(NH_4)_2C_2O_4$; (6) NaF; (7) $Na_2S_2O_3$, and warm; (8) H_2O_2; (9) $K_4FeC_6N_6$; (10) Na_2HPO_4; (11) KIO_3; (12) K_2CrO_4; (13) sebacic acid; (14) Cl or Br upon the suspended hydroxides; (15) K_2SO_4 to saturation. Try also the action of acetic and dilute hydrochloric acids upon the precipitates formed in (1), (2), (4), (10), (11), and (12), and the action of H_2O_2 upon the hydroxides.

TABLE III.

If rare earths are to be tested for, treat the hydrochloric acid solution of the Fe and Al group precipitate with NaF.* This precipitates the fluorides of the rare and possibly the alkali earths. The precipitate should be thoroughly washed, and evaporated with H_2SO_4 to decompose the fluorides. This process removes the alkali earths as insoluble sulphates. The solution containing the sulphates of the rare earths, with excess of H_2SO_4 removed, is treated with $Na_2S_2O_3$, and warmed.

P	F	
$Th(S_2O_3)_2$.	Ce and Y earths.	
Dissolve in HCl.	Saturate with Na_2SO_4.	
Precipitate with $H_2C_2O_4$, wash thoroughly.	P	F
Dissolve in $(NH_4)_2C_2O_4$, acidify with HCl.	$xCe_2(SO_4)_3 \cdot yNa_2SO_4$.	Add NH_4OH; white P, which dissolves in acid, and is pptd. by $(NH_4)_2C_2O_4$ = Y.
P confirms Th.	Decompose with NaOH,† and add H_2O_2.	
	Reddish yellow = Ce.‡	

---

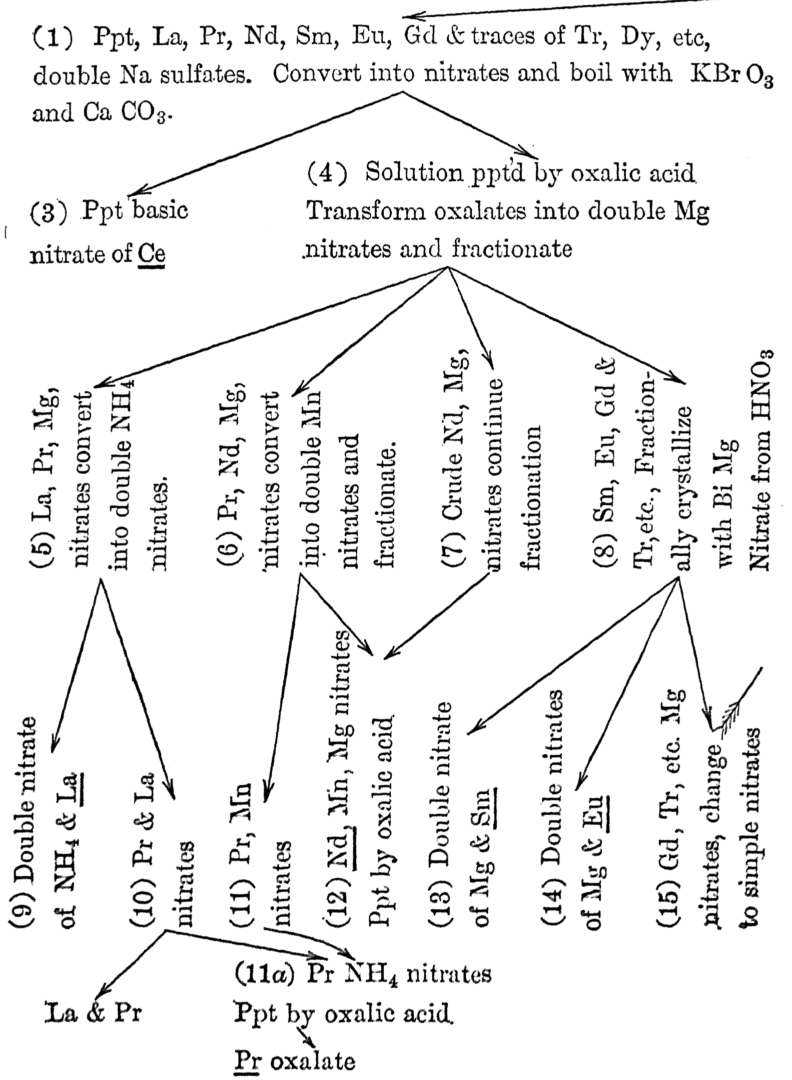
* Noyes, Bray, and Spear evaporate the HCl solution of the Al and Fe group to dryness and treat with HF. They state that the fluorides of Al and Cr are somewhat insoluble in HF, and that Ti and Zr, if present, tend to retain HF.

† The double sulphates may be conveniently decomposed by fusion with an equal weight of pure charcoal (sugar carbon) in a porcelain crucible. The residue after fusion, consisting mainly of sulphides, dissolves readily in dilute HCl (Browning and Blumenthal, Amer. Jour. Sci. [4] XXXII, 164).

‡ If the presence of other Ce earths is suspected, they may be removed from Ce by treating the hydroxides suspended in a solution of NaOH with Cl or Br. These earths dissolve, leaving CeO_2.

TABLE

CHLORIDES OF La, Ce,



(1) Ppt, La, Pr, Nd, Sm, Eu, Gd & traces of Tr, Dy, etc, double Na sulfates. Convert into nitrates and boil with KBrO_3 and Ca CO_3.

(3) Ppt basic nitrate of Ce

(4) Solution pptd by oxalic acid Transform oxalates into double Mg nitrates and fractionate

(5) La, Pr, Mg, nitrates convert into double NH_4 nitrates.

(6) Pr, Nd, Mg, nitrates convert into double Mn nitrates and fractionate.

(7) Crude Nd, Mg, nitrates continue fractionation

(8) Sm, Eu, Gd & Tr, etc., Fractionally crystallize with Bi Mg Nitrate from HNO_3

(9) Double nitrate of NH_4 & La

(10) Pr & La nitrates

(11) Pr, Mn nitrates

(12) Nd, Mn, Mg nitrates Ppt by oxalic acid

(13) Double nitrate of Mg & Sm

(14) Double nitrates of Mg & Eu

(15) Gd, Tr, etc. Mg nitrates, change to simple nitrates

(11*a*) Pr NH_4 nitrates Ppt by oxalic acid.

Pr oxalate

La & Pr

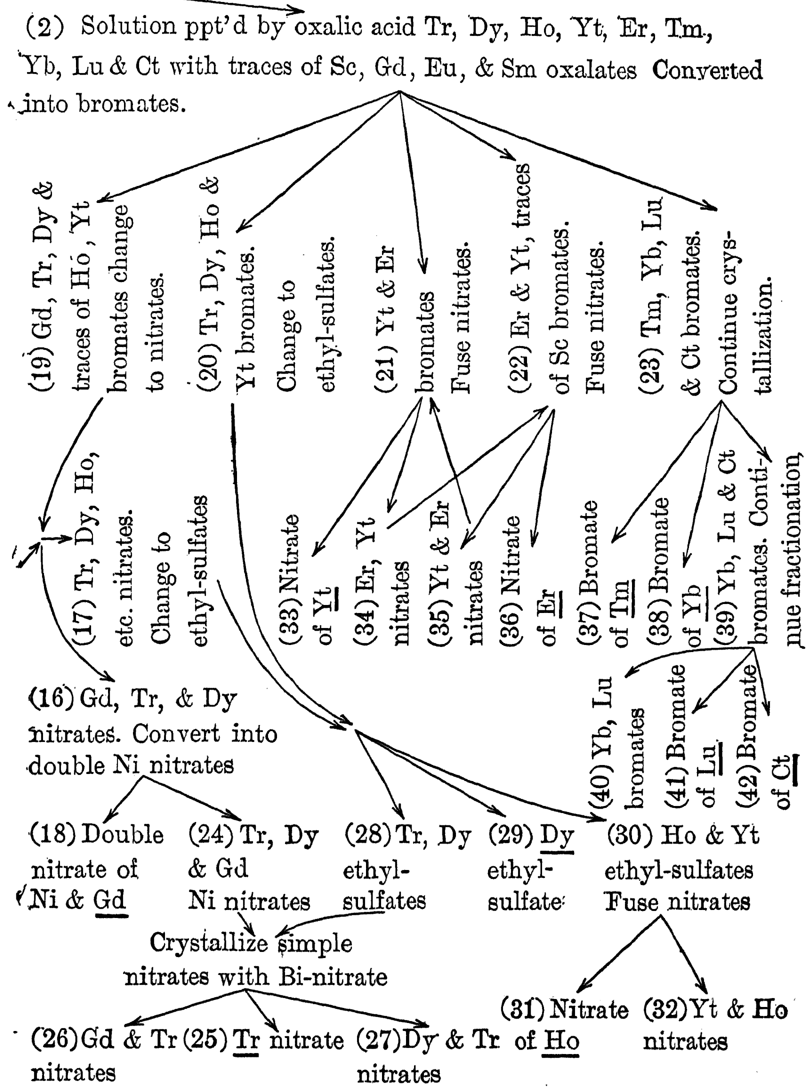
---

* This diagram, published by James in 1912 (Jour. Amer. Chem. Soc., xxxiv, 757) of Th and Zr. For descriptive details see original article.

[*By permission of the Journal of*

IV.*

Pr, ETC., + Na_2SO_4


(2) Solution ppt'd by oxalic acid Tr, Dy, Ho, Yt, Er, Tm., Yb, Lu & Ct with traces of Sc, Gd, Eu, & Sm oxalates Converted into bromates.
(19) Gd, Tr, Dy & traces of Ho, Yt bromates change to nitrates.
(20) Tr, Dy, Ho & Yt bromates. Change to ethyl-sulfates.
(21) Yt & Er bromates Fuse nitrates.
(22) Er & Yt, traces of Sc bromates. Fuse nitrates.
(23) Tm, Yb, Lu & Ct bromates. Continue crystallization.
(17) Tr, Dy, Ho, etc. nitrates. Change to ethyl-sulfates
(33) Nitrate of Yt
(34) Er, Yt nitrates
(35) Yt & Er nitrates
(36) Nitrate of Er
(37) Bromate of Tm
(38) Bromate of Yb
(39) Yb, Lu & Ct bromates. Continue fractionation
(40) Yb, Lu bromates
(41) Bromate of Lu
(42) Bromate of Ct
(16) Gd, Tr, & Dy nitrates. Convert into double Ni nitrates
(18) Double nitrate of Ni & Gd
(24) Tr, Dy & Gd Ni nitrates
(28) Tr, Dy ethyl-sulfates
(29) Dy ethyl-sulfate
(30) Ho & Yt ethyl-sulfates Fuse nitrates
Crystallize simple nitrates with Bi-nitrate
(31) Nitrate of Ho
(32) Yt & Ho nitrates
(26) Gd & Tr nitrates
(25) Tr nitrate
(27) Dy & Tr nitrates

brings the problem of rare earth separation to date. It assumes the previous removal

the American Chemical Society and the Author.]

TABLE V.*

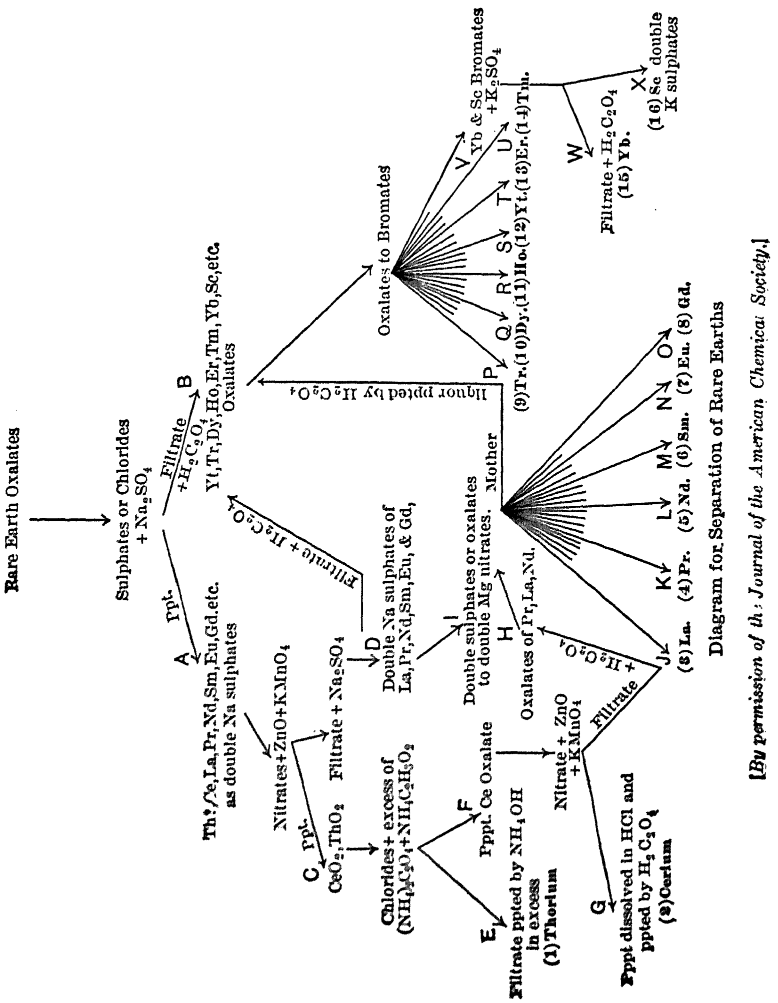

Rare Earth Oxalates
Sulphates or Chlorides + Na_2SO_4
Ppt.
Filtrate $+H_2C_2O_4$
A
Th, Ce, La, Pr, Nd, Sm, Eu, Gd, etc. as double Na sulphates
B
Yt, Tr, Dy, Ho, Er, Tm, Yb, Sc, etc. Oxalates
Nitrates+ZnO+$KMnO_4$
C
Ppt.
CeO_2, ThO_2
Filtrate + Na_2SO_4
Filtrate + $H_2C_2O_4$
D
Double Na sulphates of La, Pr, Nd, Sm, Eu, & Gd,
Chlorides + excess of $(NH_4)_2C_2O_4+NH_4C_2H_3O_2$
F
Fppt. Ce Oxalate
E
Filtrate ppted by NH_4OH in excess (1) Thorium
Nitrate + ZnO + $KMnO_4$
G
Fppt dissolved in HCl and ppted by $H_2C_2O_4$ (2) Cerium
Filtrate
I
Double sulphates or oxalates to double Mg nitrates.
H
Oxalates of Pr, La, Nd,
+ $H_2C_2O_4$
Mother liquor ppted by $H_2C_2O_4$
Oxalates to Bromates
P Q R S T U
(9) Tr. (10) Dy. (11) Ho. (12) Yt. (13) Er. (14) Tm.
V
Yb & Sc Bromates $+K_2SO_4$
W
Filtrate + $H_2C_2O_4$ (15) Yb.
X
(16) Sc double K sulphates
J K L M N O
(3) La. (4) Pr. (5) Nd. (6) Sm. (7) Eu. (8) Gd.

Diagram for Separation of Rare Earths

[*By permission of the Journal of the American Chemical Society.*]

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* This diagram, published by C. James in 1908 (Jour. Amer. Chem. Soc., xxx, 979) will serve to give a satisfactory idea of the best methods in use, at the time of its publication, for the detailed separation of the rare earths. For details reference is made to the original paper.

IV.

SILVER, COPPER AND TIN GROUP.

Before taking up the analysis outlined in Table VI, the student is directed to review the reactions of the rare elements involved. Lead, mercury, and arsenic are included for purposes of comparison. Taking separate portions of solutions of the following compounds, $Pb(NO_3)_2$, $TlNO_3$, $HgCl_2$, $AuCl_3$, H_2PtCl_6, H_2SeO_3, H_2TeO_3, K_3AsO_3, and $(NH_4)_2MoO_4$, make the following experiments, and record the results in tabular form: (1) Add HCl; (2) add hot water to any precipitate formed in (1); (3) add H_2SO_4 to solutions of Pb and $\overset{\mathrm{I}}{\mathrm{Tl}}$; (4) add KI to solutions of Pb and $\overset{\mathrm{I}}{\mathrm{Tl}}$; (5) add H_2S to separate solutions of all the salts mentioned above; (6) add $(NH_4)_2S$ to all sulphides precipitated in (5); (7) add HNO_3(1:3) to the sulphides of Hg, Pb, Pt, and Au; (8) add Br water and KCl to the sulphides of Hg, Pt, and Au; (9) add NaOH and $H_2C_2O_4$ to solutions of Au and Hg and warm; (10) acidify with HCl the sulpho salts of As, Pt, Au, Se, Te, and Mo; (11) add HCl, then $KClO_3$ to the sulphides of As, Pt, Au, Se, Te, and Mo; (12) add HCl, then Na_2SO_3 to solutions of Se, Te, and Mo; (13) add KI to solutions of Te and Mo; (14) to a solution containing Mo add Zn+KSCN and enough HCl to start evolution of H_2.

DIRECTIONS AND NOTES FOR Ag, Cu, AND Sn GROUP.

Add 4 $\overline{\mathrm{cm.}}^{3}$ of HCl (dilute). Filter, wash with cold water (about 10 $\overline{\mathrm{cm}}^{3}$). Test the filtrate for traces of Tl and Pb.

$PbCl_2$ and TlCl are somewhat soluble in cold water (20–40 mgs. of $PbCl_2$ and 5–15 mgs. of TlCl may remain in solution). The solubility of these chlorides in water is decreased by the presence of HCl in moderate amount.

Ag Group.—Treat the precipitate of AgCl, $PbCl_2$, and TlCl with 10 $\overline{\mathrm{cm.}}^{3}$ of boiling water, pouring it back and forth several times. Treat the hot water extract containing Pb and Tl with one-fifth its volume of strong H_2SO_4, allow to cool and stand a few minutes. Wash with dilute H_2SO_4, since $PbSO_4$ is slightly soluble in water. To the solution containing Tl add 2–3 $\overline{\text{cm.}}^3$ of 1% KI. If free I appears, add H_2SO_3. Yellow TlCI indicates Tl.

TlI is more insoluble than TlCl. Its solubility is decreased by KI. $\overset{\text{I}}{\text{Tl}}$ is oxidized to $\overset{\text{III}}{\text{Tl}}$ by Cl, Br, I, and aqua regia. $\overset{\text{III}}{\text{Tl}}$ is reduced by H_2SO_3. $\overset{\text{I}}{\text{Tl}}$ is slightly oxidized by HNO_3. $\overset{\text{III}}{\text{Tl}}$ is not precipitated by HCl.

Cu and Sn Group.—Before adding H_2S see that the volume of the solution is about 40 $\overline{\text{cm.}}^3$ of which 4 $\overline{\text{cm.}}^3$ is HCl (1 . 12). Heat the solution to boiling, and saturate with H_2S. Use a flask fitted with stopper and delivery tubes, so that gentle pressure can be obtained. After saturating, add equal volume of water, cool, saturate again.

H_2S is passed at boiling temperature for $\overset{\text{V}}{\text{As}}$, Pt, and Mo. Pressure is used to precipitate Pt metals and Mo. The small volume of liquid, 40 $\overline{\text{cm.}}^3$, is to keep Ti, Bi, and Sb from precipitating as hydroxides or basic salts, and to precipitate As more readily. The final dilution and cooling is to precipitate all of the Cd, Pb, and $\overset{\text{II}}{\text{Sn}}$.

Digest precipitate with 10–20 $\overline{\text{cm.}}^3$ of $(NH_4)_2S$, add equal volume of water, filter, and wash.

MoS_{2-3} dissolves in moderate amount of $(NH_4)_2S$ and gives a deep orange-red color to solution. Its presence in Cu Group does not interfere. PtS_2 is not completely dissolved by $(NH_4)_2S$.

Cu Group.—Add 10–20 $\overline{\text{cm.}}^3$ HNO_3 (one-third strength), boil gently a few minutes. Dissolve residue in 10–40 $\overline{\text{cm.}}^3$ of saturated bromine water. Cover dish and warm 5–10 minutes. Expel excess of bromine, add 0.5 grm. KCl, 1–2 $\overline{\text{cm.}}^3$ HCl (1 . 12). Evaporate until KCl crystallizes, cool, add water until KCl dissolves. Filter, wash with KCl. Yellow K_2PtCl_6 = Pt. Dissolve in hot water, test by KI. Make filtrate alkaline with 10% NaOH, add saturated solution of $H_2C_2O_4$ to acidity, dilute to 15 $\overline{\text{cm.}}^3$ and warm 10–15 minutes on steam bath. Purple or dark yellow = Au.

K_2PtCl_6 is much less soluble in KCl than in water. Color with KI due to K_2PtI_6. Au is precipitated readily by $H_2C_2O_4$ only when solution is slightly acid and hot. Precipitation takes place slowly.

Sn Group.—Dilute the $(NH_4)_2S$ solution, acidify with HCl and warm gently; drain as dry as possible on a filter and warm with HCl (1 . 20), which removes Sn and Sb. Warm with 5–10 $\overline{\text{cm.}}^3$ HCl (1 . 12), add a little $KClO_3$, evaporate to 2 $\overline{\text{cm.}}^3$, or until KCl crystallizes out (see test for Pt, Cu Group). After removing Pt, remove As by NH_4OH and $MgCl_2$ mixture. To the filtrate add some $H_2C_2O_4$, boil out NH_3, make slightly acid with $H_2C_2O_4$, and test for Au as in Cu Group. Evaporate filtrate from Au nearly to dryness, add 10 cm.^{3} HCl, and if KCl separates filter it off. Add 0.2 grm. Na_2SO_3 and allow to stand a few minutes, adding more $NaSO_3$ if odor of SO_2 is not distinct. Red Se = Se.

Reaction more delicate in cold because red, not black, Se forms. Te is reduced by Na_2SO_3 if HCl is much more dilute than 1 . 12.

Dilute filtrate from Se, add equal volume of water, a little KI solution, and Na_2SO_3. Black Te = Te. Filter after a few minutes.

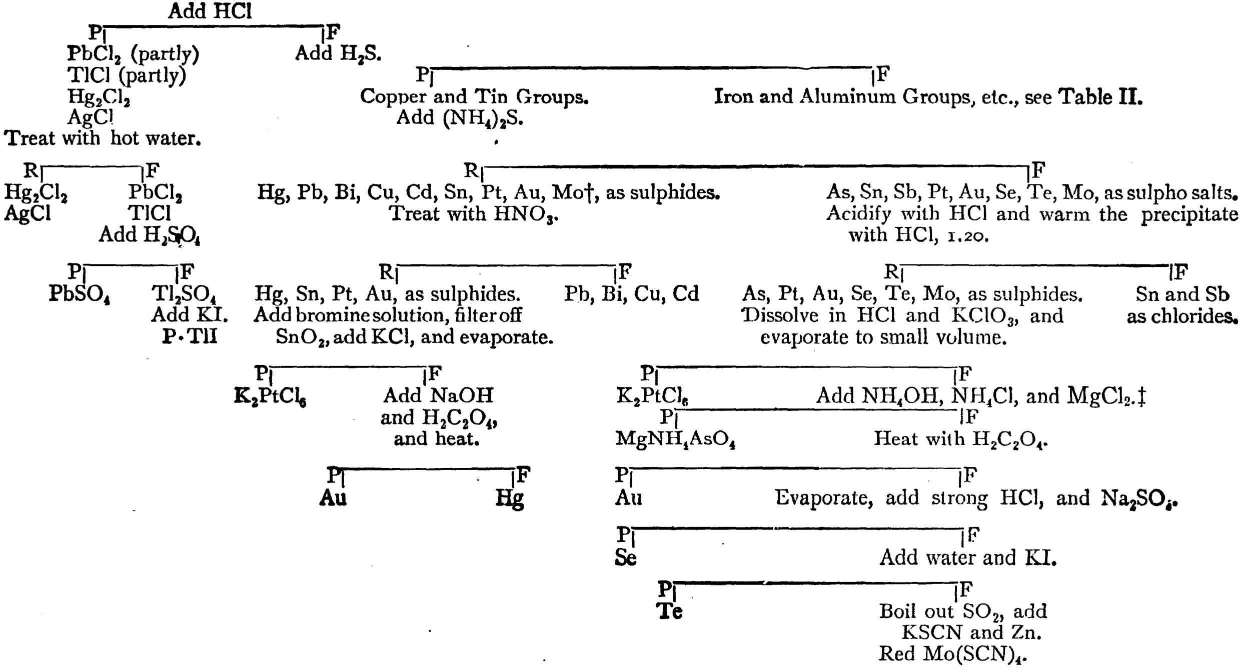
KI is added because TeI_4 is more readily reduced by SO_2 than is $TeCl_4$. Molybdic acid is slowly reduced by HI with liberation of I; therefore Te should be filtered off before confused with this color.

Boil filtrate from Te until SO_2 is expelled. Add a little 10% KSCN and some Zn. Red color = Mo.

The SO_2 is boiled out to avoid precipitation of S by Zn. Long continued action of Zn will cause bleaching of red color.

TABLE VI.*

SILVER, COPPER, AND TIN GROUPS.



Add HCl

- P: $PbCl_2$ (partly), $TlCl$ (partly), Hg_2Cl_2, $AgCl$. Treat with hot water.
  - R: Hg_2Cl_2, $AgCl$
  - F: $PbCl_2$, $TlCl$. Add H_2SO_4.
    - P: **$PbSO_4$**
    - F: Tl_2SO_4. Add KI. **P·TlI**
- F: Add H_2S.
  - P: Copper and Tin Groups. Add $(NH_4)_2S$.
    - R: Hg, Pb, Bi, Cu, Cd, Sn, Pt, Au, Mo†, as sulphides. Treat with HNO_3.
      - R: Hg, Sn, Pt, Au, as sulphides. Add bromine solution, filter off SnO_2, add KCl, and evaporate.
        - P: **K_2PtCl_6**
        - F: Add NaOH and $H_2C_2O_4$, and heat.
          - P: **Au**
          - F: **Hg**
      - F: Pb, Bi, Cu, Cd
    - F: As, Sn, Sb, Pt, Au, Se, Te, Mo, as sulpho salts. Acidify with HCl and warm the precipitate with HCl, 1.20.
      - R: As, Pt, Au, Se, Te, Mo, as sulphides. Dissolve in HCl and $KClO_3$, and evaporate to small volume.
        - P: K_2PtCl_6
        - F: Add NH_4OH, NH_4Cl, and $MgCl_2$.‡
          - P: $MgNH_4AsO_4$
          - F: Heat with $H_2C_2O_4$.
            - P: Au
            - F: Evaporate, add strong HCl, and **Na_2SO_3**.
              - P: **Se**
              - F: Add water and KI.
                - P: **Te**
                - F: Boil out SO_2, add KSCN and Zn. Red $Mo(SCN)_4$.
      - F: Sn and Sb as chlorides.
  - F: Iron and Aluminum Groups, etc., see **Table II.**

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* Before making use of this table the student should carefully study the original article (Noyes and Bray, Jour. Amer. Chem. Soc., XXIX, 137).

† Amount present negligible.

‡ On account of the possibility of precipitating some magnesium tellurite at this point, it is recommended that the test for arsenic be deferred until after the removal of the tellurium. See next page.

Modification of the method described in Table VI as applied to the separation of platinum, gold, selenium, tellurium, arsenic, and molybdenum.*

The filtrate from the K_2PtCl_6 (see previous page) should be made faintly alkaline with NaOH and the Au precipitated either by H_2O_2 or by acidifying with oxalic acid and warming. The Se is precipitated as in Table VI.

Treat filtrate with Na_2SO_3+KI.

P
Te

F
Treat by boiling to remove the SO_2, by H_2O_2 to break up the iodide, by boiling to remove iodine, by excess of NaOH and H_2O_2 to oxidize the arsenic to arsenate, by acidifying to remove excess of NaOH, by NH_4OH and $MgCl_2$ mixture, and filtration.

P
NH_4MgAsO_4
Confirm by $AgNO_3$, forming red-brown Ag_3AsO_4.

F
Test for Mo by KSCN and Zn in HCl. Red $Mo(SCN)_4$.

---

* Browning, Simpson and Porter, Am. Jour. Sci. XL, 349; XLII, 106.

TABLE VII.*

Add HCl.

- P: **Ag, Hg_2, Pb, Tl, as chlorides.** H_2SiO_3, SbOCl, partly. H_2WO_4. Treat with boiling water.
  - R: Add HCl in sufficient amount to remove SbOCl as $SbCl_3$. Wash with water and warm with NaOH in excess.
    - R: **Reject.**
    - F: Na_2SiO_3 Na_2WO_4 Acidify with HCl.
      - P: **Remove H_2SiO_3** by HF. R. **H_2WO_4.**
      - F: Reject.
  - F: Pb, Tl, as chlorides. Add H_2SO_4. See Table I.
    - P: Pb
    - F: Tl
- F: Add H_2S.
  - P: **Hg,** Pb, Bi, Cu, As, Sb, Sn, Se, Te, Au, Pt, Mo, as sulphides or elements with sulphur, e.g., Se and Te. For separation see Table I.
  - F: Test for H_3PO_4 **and organic matter,** and if present remove. Add NH_4Cl, NH_4OH, and **$(NH_4)_2S$.**
    - P: Fe, Ni, Co, Mn, Zn, U, as sulphides. Al, Cr, Ti, Be, and rare earths, as hydroxides. Wash with water containing $(NH_4)_2S$ and treat with cold double normal HCl.
      - R: Co, Ni, as sulphides.
      - F: Rare earths, Fe, Al, Cr, Mn, Zn, **U, Be, Ni** (traces). Evaporate to small volume, oxidize with **1–2** cm^3. of HNO_3, **and add NaOH in excess.**
        - P: Rare earths, Fe, Cr, Mn, U, Be (traces). Dissolve in HCl and add oxalic acid to warm acid solution.
          - P: Rare earth oxalates. Traces of Fe, Cr, Mn, U. Boil with concentrated $(NH_4)_2C_2O_4$.
            - R: **Ce earth** and Y earth oxalates. **Boil** with NaOH. Dissolve in dilute HNO_3, add alcohol to reduce Ce^{III} salt. Allow to stand over night with solid K_2SO_4.
              - R: **Ce** earth double potassium sulphates, Th (traces). **Boil** with NaOH, wash, and treat the suspended hydroxides, in the presence of NaOH, with Cl.
                - R: **Ce oxyhydroxide.**
                - F: Distinguish by spectrum analysis. See also Tables III, IV, and V.
              - F: Y earths. Precipitate by NH_4OH. Dissolve in HNO_3, and identify by spectroscopic methods. See also diagram, **p. 45.**
            - F: Th, Zr, as double ammonium oxalates. Acidify with HCl.
              - P: $Th(C_2O_4)_2$.
              - F: Evaporate and ignite. ZrO_2 should dissolve in **HF.**
          - F: Fe, Cr, Mn, U, Zr (traces).
        - F: Al, Be, Zn, as sodium salts. Acidify with HCl, add NH_4OH in excess.
          - P: Al, Be, as hydroxides. Dissolve in HCl and boil with $NaHCO_3$.
            - P: $Al(OH)_3$
            - F: Be
          - F: Zn.
    - F: Alkali earths and alkalies. See Table IV.

---

* Method of Böhm (Darstellung der seltenen Erden, Vol. II, p. 134) somewhat amplified and diagrammatically arranged.

V.

THE TUNGSTEN GROUP.

Before taking up the analysis as outlined in Table VIII, the student is instructed to review the reactions of the elements considered.

Taking separate solutions of the following salts, Na_2SnO_3, Na_2SiO_3, Na_2WO_4, $K_8Ta_6O_{19}$ and $K_8Nb_6O_{19}$, try the action of the following reagents, and record the results in tabular form: (1) HNO_3 to acid reaction; effect of excess and result on evaporation; (2) HCl and H_2SO_4 under the same conditions as in (1); (3) NaOH, KOH or NH_4OH upon the freshly precipitated oxide or hydroxide; (4) Zn+HCl on solutions of Ta, Nb, and W; (5) H_2S on solutions containing Ta, Nb, W, Sn and Si, and subsequent acidification with HCl; (6) $NaPO_3$ bead with and without $FeSO_4$, upon small particles of the oxides or hydroxides. Try also the effect of warming the dried oxides with HF in a lead dish.

TABLE VIII.*

Dissolve in HF, add H_2SO_4, and evaporate to the fuming-point to remove SiF_4; cool, pour into 5 $\overline{\text{cm.}}^3$ of water, add NH_4OH to alkaline reaction, then colorless $(NH_4)_2S$, and warm in a covered dish at 60° C. for 15 minutes.

P	F
Ta_2O_5, Nb_2O_5, (TiO_2), (WO_3). Warm with H_2O_2 and HCl.	$(NH_4)_2SnS_3$, $(NH_4)_2WS_4$. Acidify with H_2SO_4, shake and filter.

R	F	R	F
Ta_2O_5. Dissolve in HF, add K_2CO_3, and boil. $2K_2TaF_7$, Ta_2O_5 indicates Ta.	$NbCl_5(TiO_2)(WCl_6)$. Evaporate with H_2SO_4, dilute, pour through a Zn column, add $HgCl_2$. Ppt. Hg_2Cl_2 indicates Nb.	SnS_2. (WS_2).	H_2WO_4. Confirm by Zn+HCl. Blue color indicates W.

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* Abridged and adapted from A. A. Noyes, Technology Quarterly, Vol. XVII, No. 2, 214.

VI.

THE PLATINUM GROUP.

Before attempting any separations by the use of Table IX, the student is directed to review the reactions of the platinum group.

Take separate portions of solutions of H_2PtCl_6, Na_2IrCl_6, K_2OsCl_6, $RuCl_3$, Na_3RhCl_6, and $PdCl_2$ and try the action of the following reagents upon them, recording the results in tabular form: (1) H_2S; (2) $(NH_4)_2S$ upon the sulphides precipitated; (3) KOH or NaOH; (4) KCl or NH_4Cl; (5) KNO_2; (6) Na_2O_2; (7) Zn + HCl.

The separation of the platinum metals is one of the most difficult analytical problems. The following scheme, offered by Leidie and Quennessen (Bull. Soc. Chim. xxvii, 181 (1902)), has been found to give fairly satisfactory results when the mixtures examined were not especially complex.

TABLE IX.

The finely divided metals are mixed with 5 to 6 times their weight of Na_2O_2 and heated gently in a nickel crucible. Treat with water.

R

The residue contains Ni, Pt, and Rh, as insoluble compounds. Treat with hot HCl, filter, evaporate excess of acid, add $NaNO_3$ and Na_2CO_3 to neutrality, and boil.

P

Ni removed.

F

Add excess of HCl, evaporate to dryness. Add water and NH_4Cl.

P

Pt as chloroplatinate

F

Rh in solution as reddish double chloride.

F

The filtrate contains soluble sodium salts of Os, Ru, Ir, and Pd.
Yellow solution = Os, Ru, or Pd.
Blue solution = Ir.
Colorless solution = absence of all.

(*a*) If solution is yellow, pass chlorine and heat, catching distillate in cold water.

R

The residue when neutralized with HCl and evaporated with NH_4OH and KCl should give red crystals of potassium chlorpalladate if Pd is present.

D

(1) If either Os or Ru is present, NH_4SH gives a black sulphide.

(2) If Os is present a violet osmate is produced by KNO_3 and heating.

(3) If Ru is present a black ppt. of Ru is produced by KOH and alcohol in the cold.

(*b*) If solution is blue, neutralize with HCl, evaporate in presence of NH_4OH and KCl. Black crystals of potassium chlor-iridate = Ir.

CHAPTER XIV.

SPECTROSCOPIC TABLES.

THE importance of spectrum analysis in the chemistry of the rarer elements has suggested the insertion of some spectroscopic charts and tables.

In order to make possible the location with a fair degree of certainty of the lines in the field of visible spectra, the wave lengths of the Fraunhofer lines shown in spectrum No. 1, on the chart of Flame Spectra, are here given:

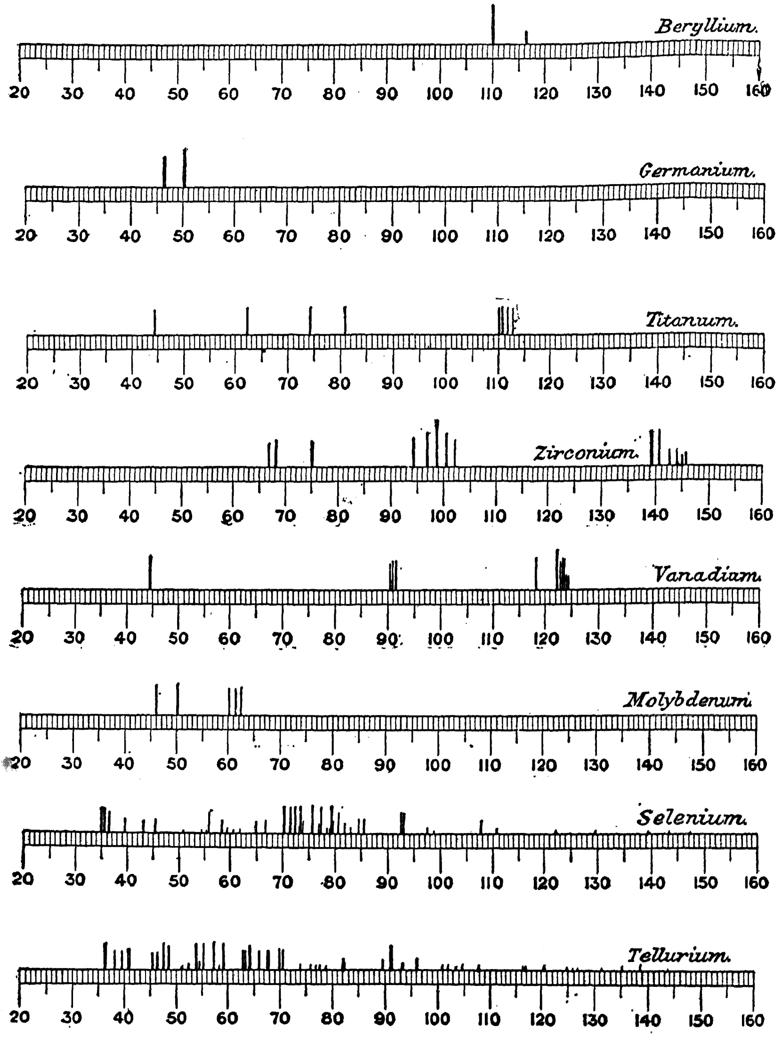
A = 7594; B = 6867.4; C = 6563; D = 5893.1; E = 5270;
b = 5172; F = 4861.4; G = 4308; H = 3968.6; H_1 = 3933.8.

A comparison of these lines with the arbitrary scale given in the charts of Flame and Spark Spectra will serve to locate the position of the various spectra.

In the table of Chief Lines only a few of the more important are recorded. The figures in parenthesis, e. g. Li (3232–6708), show the range of the chief lines as given by Exner and Haschek. The second number, (6), gives the total number of chief lines. The other numbers, 4202.2, 4603.1, 6103.8, 6708.1, indicate the lines of greatest intensity. Few lines of an intensity below 10 on the scale used by these investigators are mentioned, and those in heavy type are of an intensity of 50 or above.

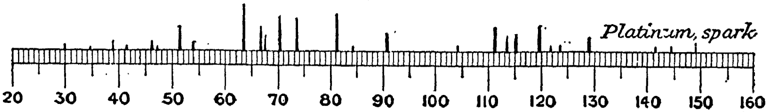
The visible spectrum lies between 7600 and 4000; the lines outside of these limits, non-existent to the eye, are observed by other methods, photography being especially valuable for this purpose whenever it is applicable. Many of the principal lines of the rare element spectra will be seen to be of a wave length below 4000, and therefore to lie in the ultra violet.

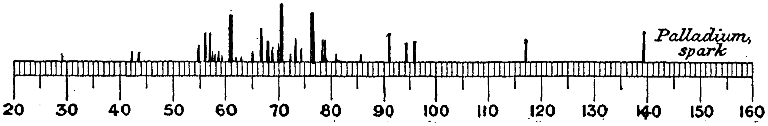
TYPICAL SPARK SPECTRA.

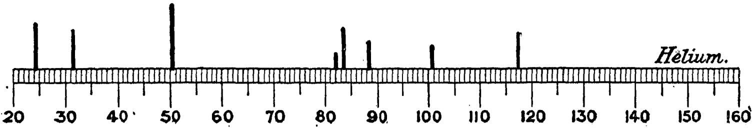


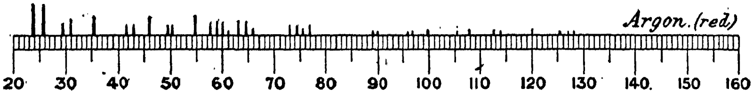
Selected from An Introduction to the Study of Spectrum Analysis, Watts. Longmans, Green, & Co. (1904).

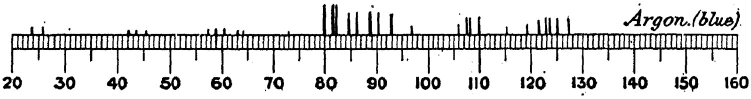
TYPICAL SPARK SPECTRA.

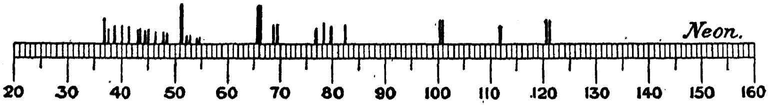


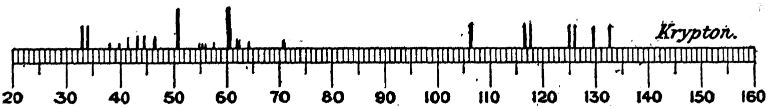


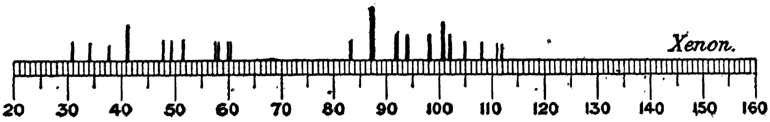




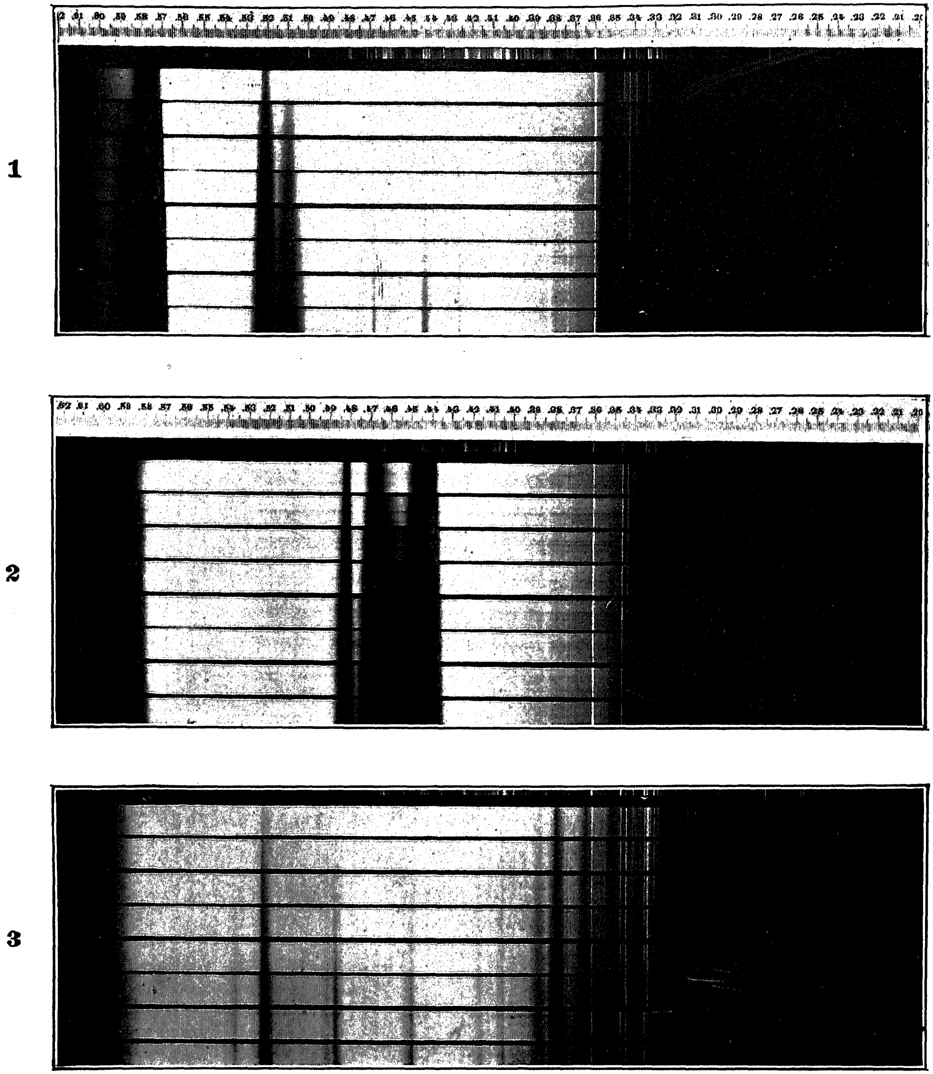








TYPICAL ABSORPTION SPECTRA.

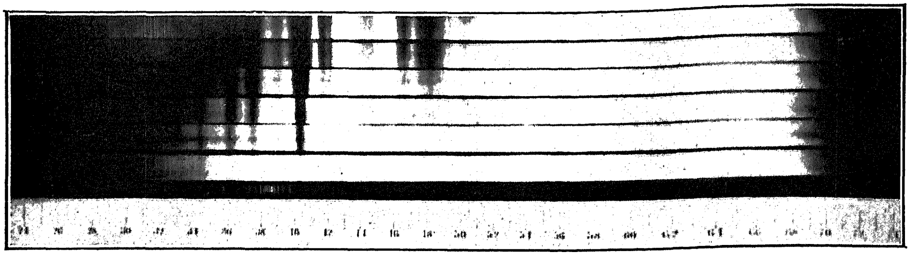


1. Neodymium-Ammonium Nitrate. 2. Praseodymium-Ammonium Nitrate.
3. Erbium Chloride.

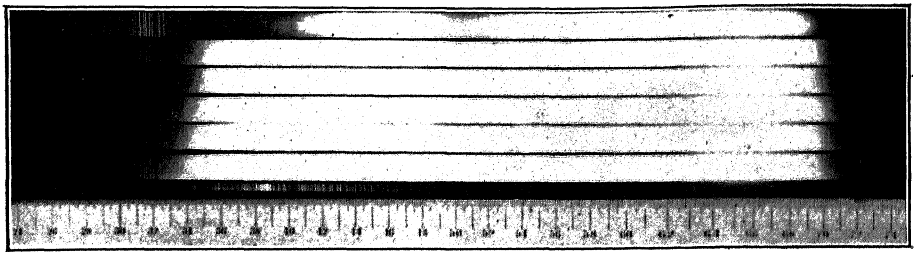
From *Atlas of Absorption Spectra*, by Uhler and Wood, Carnegie Publication, No. 71.

TYPICAL ABSORPTION SPECTRA.

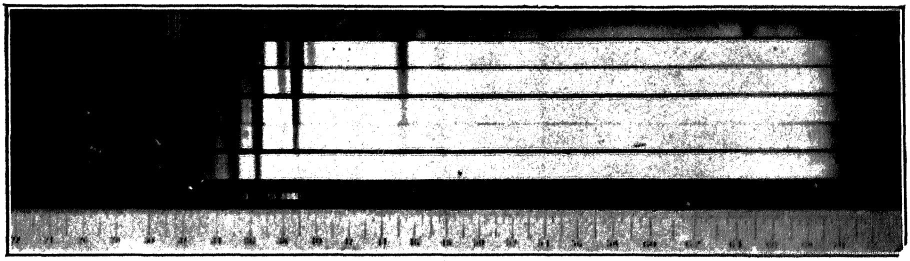
1



2



3



1. Samarium Chloride. 2. Gadolinium Chloride. 3. Dysprosium Chloride

From plates accompanying *The Absorption Spectra of Solutions of Comparatively Rare Salts*, by Jones and Strong, Carnegie Publication, No. 160.

CHIEF LINES IN ARC AND SPARK SPECTRA.*

Element.	Arc Spectrum.	Spark Spectrum.
Beryllium	(2650–3321)(5) 2650.7, 3130.5, 3131.1, 3321.2, 3321.5	(2494–4572)(5) 3130.5, 3131.2 (4428, 4709, 5056.4) †
Cæsium	(4555–6723)(3) **4555.5, 4593.3**, 6723.6	(4277–4603)(3) 4277.2, 4603.9
Celtium	(2450–3700) ‡ 2685.2, 2765.8, 3080.7, 3118.6, 3197.9	
Cerium	(3952–6371)(23) 4337.9, 4386.9, 4527.5, 4594.1	(3801–4628)(14) 4460.3, 4562.5, **4572.4, 4594.1**, 4628.3
Dysprosium	(3524–4957)(19) 4168.1, 4187, 4211.8, 4957.5	(3454–4078)(16) 3138.8, 4000.6
Erbium	(3312–6221)(34) 3692.8, 3896.4, 3906.4, 4151.2	(3372–4675)(6) 3499.2, 3692.8, 3906.5, 4419.7
Europium	(3688–6645)(14) **4129.9, 4205.2, 4435.7, 4594.2, 4627.4**	(3725–6645)(11) **3930.6, 3972.1, 4129.9, 4205.2, 4435.7**
Gadolinium	(3082–6114)(34) 4130.6, 4251.9, 4262.2, 4327.3, 4342.3	(2628–4540)(24) 3422.6, 3664.7, 3768.5
Gallium	(2874–6397)(5) 2874.3, 2943.7, 4033.2, 4172.2	(4033–4172)(4) 4033.1, 4172.2
Germanium	(2592–3269)(8) 2651.3, 2709.7, 2754.7, **3039.2**	(2592–4226)(8) 2754.6, 3039.2, 4179.2, **4226.7**, 426.
Gold	(2676–4792)(4) 2676, 3122.9, 4792.8	(2428–4792)(5) 2428, 2676, 2802.3
Indium	(3039–4511)(5) **3256.2, 4101.9, 4511.5**	(2941–4511)(6) **4102, 4511.5**
Iridium	(2924–3800)(14) 3220.9, 3368.6, 3513.8, 3800.2	(2833–4399)(13) 3606, 3800.2, 3976.4, 4399.7
Lanthanum	(3949–6394)(7) 3949.2, 4238.5, 6250.1, 6262.5, 6394.4	(3171–4522)(16) **3517.2, 3791, 3794.9, 3949.2**, 4123.3, 4522,5

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* According to Exner and Haschek, Die Spektren der Elemente bei Normalen Druck.

† See Lecoq de Boisbaudran, Compt. rend., CLIII, 318. ‡ See Urbain, Compt. rend., CLII, 141.

CHIEF LINES IN ARC AND SPARK SPECTRA—*Continued.*

Element.	Arc Spectrum.	Spark Spectrum.
	(3232–6708)(6)	(4602–6708)(4)
Lithium	**4602.2, 4603.1, 6103.8, 6708.1**	**6103.8, 6708.1**
(Aldebaranium)	(3031–5556)(8)	(2803–4786)(15)
Lutecium	**3289.5, 3694.3, 3988.1**	**3289.5, 3694.3**
	(3132–6030)(16)	(2644–6030)(15)
Molybdenum	**3798.4, 3864.3,** 3903.1, 5533.2, 6030.8	3864.2, 5506.7, 5533.2, 6030.8
	(3868–6385)(22)	(4012–4463)(9)
Neodymium	3951.3, 4061.2, 4303.7, 4325.8, 6385.3	4303.7, 4446.5, 4451.6, 4463.1
	(3399–4254)(14)	(2936–3891)(18)
Neoholmium *	3456.1, 3748.3, 3891.1	3399.1, 3456.1, 3556.9, 3891.1
(Cassiopeium)	(2615–6463)(30)	(2603–4184)(16)
Neoytterbium	**3507.5, 4184.4, 5476.8, 6222.1**	**2772.7, 2911.5, 3077.7, 3397.1, 3554.5**
	(3713–5344)(28)	(2927–4672)(14)
Niobium	**4059.1,** 4079.8, 4101.1	3094.3, 4059.1, 4630.3, 4672.2
	(3752–4420)(11)	(2909–4420)(5)
Osmium	3782.3, 4135.9, 4212, 4420.6	4420.6
	(3028–6784)(27)	(2776–4213)(13)
Palladium	**3404.7, 3517, 3609.7, 3634.8**	3404.8, **3609.7,** 3634.8, 4213.1
	(2659–4521)(14)	(2424–4552)(8)
Platinum	2659.6, 2998, **3064.8,** 4498.9	2659.5, 3923.1, 4498.9, 4552.6
	(4008–4510)(14)	(3877–4510)(15)
Praseodymium	4206.8, 4223.1, 4429.3, 4496.6	4100.8, 4206.8, 4223.2, 4225.5, 4429.4
	(3280–5983)(27)	(2910–4375)(12)
Rhodium	**3323.2, 3396.9, 3502.6, 3658.1, 3692.5**	3692.5, 3799.4, 3822.4, 3856.6, 4375
	(3814–4826)(4)	(3814–4826)(3)
Radium	**3814.6, 4682.4, 4826.1**	**3814.6, 4682.4**
	(3587–6298)(4)	(3940–4294)(7)
Rubidium	**4202, 4215.7**	3940.6, 4201.9, 4244.5
	(3417–4080)(7)	(2402–4554)(18)
Ruthenium	3436.8, **3499,** 3593.1, 3596.3	2678.8, 2945.7 4554.7

* According to Exner and Haschek, holmium is composed of neoholmium, terbium, and dysprosium.

CHIEF LINES IN ARC AND SPARK SPECTRA—*Concluded.*

Element.	Arc Spectrum.	Spark Spectrum.
Samarium	(3739–4674)(29) 4152.3, 4424.5, 4434.5, 4642.4	(4319–4467)(5) 4391, 4424.5, 4467.4
Selenium	....	(3414–3800)(5) 3544, 3637.5, 3738.7
Scandium	(3353–6305)(21) 3907.6, 3912, 4023.8, 4247, 4314.3	(3353–4415)(17) **3572.7, 3613.9, 3630.8, 3642.9, 4247**
Tantalum	(3311–6516)(14) 6450.5, 6485.6, 6514.6, 6516.4	(2400–4682)(9) All below 10 in intensity
Tellurium	....	(2383–2530)(4) 2383.4, 2385.8
Terbium	(3324–4752)(22) 3509.3, 3848.9, 3874.3, 3977	(2659–4278)(17) 3509.3, 3848.9, 3874.3, 3977, 4278.7
Thallium	(2709–5350)(9) **3519.3, 3775.8, 5350.7**	(3519–5350)(7) 3519.3, 3775.8, 5350.6
Thorium	(3188–6462)(13) 4863.3, 4919.9	(2441–4391)(10) 3221.4, 3300.6, 4382.1, 4391.1
Thulium	(3131–4481)(21) 3762, 3795.9, **3848.1**, 4187.7, 4481.4	(3131–4522)(16) 3131.4, 3462.3, 3762, 3795.9, 3848.1, **4522.7**
Titanium	(3371–5210)(36) 4999.6, 5014.3, 5193.1, 5210.5	(2516–4572)(21) **3685.3**, 3900.8, 4395.2, 4572.2
Tungsten	(4008–5805)(13) 5053.4, 5224.8, 5514.8, 5735.3	(2397–5648)(18) 5053.4, 5224.8, 5492.5, 5514.9
Uranium	(3932–6449)(10) 5493.1, 5528, 6449.3	(4090–5528)(16) All below 10 in intensity.
Vanadium	(3184–6090)(16) 4111.9, 4379.4, 4384.9, 4408.7,	(3093–6090)(27) 3545.3, **3556.9**, 4379.4, 4384.9, 6090.5,
Yttrium	(3216–6435)(29) 3710.4, 4077.5, 4128.5, **4375.1**	(2367–5663)(27) **3600.9, 3710.4, 3774.5, 4375.1**, 4883.9
Zirconium	(3392–6127)(21) 4687.9, 4739.6, 4772.5, 4815.8	(3392–4497)(20) 3999.1, 4149.4, 4209.2, 4380.1

REVIEW QUESTIONS.

DESCRIPTIVE PART.

(In answering these questions be prepared to write equations for all reactions.)

I.

LITHIUM, RUBIDIUM, CAESIUM.

1. (*a*) Name the particulars of chemical behavior which led to the discovery of Li. (*b*) How and under what circumstances were Rb and Cs discovered? 2. Name the chief mineral sources. 3. Are these elements found elsewhere than in minerals? Give examples. 4. Describe in full the method you employed to obtain compounds of these elements from a mineral source. 5. Discuss briefly two other methods of extraction. 6. How are the elements prepared and how do they compare in properties? Compare with Na and K in elementary condition. 7. What salts are soluble in alcohol? 8. Name two important insoluble salts of Li. 9. Describe the action of $SbCl_3$, $SnCl_4$ and $PbCl_4$ upon salts of Cs and Rb. 10. What happens (*a*) when $Na_3Co(NO_2)_6$ and (*b*) H_2PtCl_6 act upon solutions of Li, Rb, and Cs salts? 11. Compare the solubility of the chloroplatinates and the alums of Cs, Rb and K. 12. Describe the flame and spectroscopic tests for Cs, Rb and Li. 13. Classify the alkalies Li, Na, K, Rb and Cs into two groups and give reasons for the classification.

II.

BERYLLIUM AND RADIO-ELEMENTS.

1. What properties of the compounds of Be led to its discovery? 2. Name three important mineral sources. 3. How did you obtain a compound of Be from Beryl? 4. Discuss briefly two other methods of extraction. 5. Discuss briefly the preparation and properties of the element Be. 6. What happens when a solution of a salt of Be is treated with the following reagents: (*a*) NH_4OH; (*b*) NaOH or KOH; (*c*)

$(NH_4)_2CO_3$; Na_2CO_3 or K_2CO_3; (*d*) Na_2HPO_4. 7. Discuss the behavior of $Be(OH)_2$ (*a*) toward $NaHCO_3$; (*b*) toward concentrated solutions of Be salts. 8. What salts of Be are soluble in alcohol? 9. Give examples of the hydrolysis of Be salts. 10. Discuss the peculiarities of the double alkali tartrates and the basic acetates. 11. Discuss the similarities and differences of behavior of Be and Al compounds. 12. Name the five important radio-elements. 13. What do you understand by α, β and γ rays, and how are they distinguished? 14. State briefly the disintegration theory. 15. What observations led to the discovery of radium? 16. What are the chief sources of radium? 17. How is radium extracted from pitchblende residues? 18. What common element does radium resemble? 19. Give the symbols for some of the radium salts. 20. Give the chief chemical characteristics of radium salts. 21. What are some of the physiological effects?

III.

RARE EARTHS (YTTRIUM AND CERIUM GROUPS).

1. Into what groups are the rare earths classified and upon what does the classification depend? 2. Name five of the most important mineral sources of the rare earths. 3. What are the chief mineral sources of the Y group? The Ce group? 4. How did you obtain the oxalate of Y from gadolinite and the oxalate of Ce from cerite? 5. Discuss the preparation and properties of the elements Y and Ce. 6. How do the following reagents act upon soluble salts of Y and Ce: NH_4OH; Na_2CO_3; $(NH_4)_2CO_3$; NH_4F; Na_2SO_4 or K_2SO_4 to saturation; KIO_3; Na_2HPO_4; $K_4FeC_6N_6$; $H_2C_2O_4$; K_2CrO_4? 7. Starting with CeO_2 show how you would form $CeCl_3$ and $Ce(NO_3)_4$. 8. How does H_2O_2 act upon cerous salts in alkaline solution, and upon ceric salts in acid solution? 9. Discuss the reduction of ceric salts and the oxidation of cerous salts. 10. Describe a delicate test for Ce. 11. How did Mosander separate La and Di from Ce? 12. How did Welsbach separate Di into Pr and Nd? 13. Name three of the cerium earths which give absorption spectra and show by a rough diagram the main differences. 14. What important Y earth gives a distinct absorption spectrum? 15. What is the marked difference between Ce and the other Ce earths? 16. How would you separate Ce from the other Ce earths? 17. Show by a diagram the order of the discovery of the Y earths, with the names of the discoverers, the dates of the discoveries and the sources from which the earths were obtained. Make a similar diagram for the Ce earths.

IV.

THORIUM AND ZIRCONIUM.

1. Name the chief mineral sources of Th compounds. 2. Name the chief mineral source of Zr compounds. 3. How may ThO_2 be prepared from (*a*) monazite? (*b*) mantle ashes? 4. How did you obtain a Zr compound from zircon? 5. Discuss the preparation of the elements Th and Zr. 6. Compare the action of the following reagents upon soluble salts of Th and Zr: NH_4OH; NaOH; $(NH_4)_2CO_3$; Na_2CO_3; Na_2SO_4 or K_2SO_4 to saturation; Na_2HPO_4; KF; $K_4FeC_6N_6$; KIO_3; $Na_2S_2O_3$; $H_2C_2O_4$; $(NH_4)_2C_2O_4$ in excess and the addition of HCl to the product; sebacic acid. 7. What salt of Th is used largely commercially, and how is it used? 8. In what reactions does Zr resemble and in what differ from the rare earths? 9. What happens when a solution of a Zr salt is treated with Na_2HPO_4 in the presence of H_2O_2? 10. What happens when a solution of $ZrCl_4$ is shaken with ether?

V.

GALLIUM, INDIUM, THALLIUM.

1. What are the chief mineral sources of Tl compounds? 2. In what commercial waste product is Tl often found? 3. Discuss briefly the method for the extraction of Tl. How did you extract it? 4. Discuss the preparation and properties of TlCl, TlBr and TlI. 5. What happens when a solution of a thallous salt is treated with (*a*) H_2PtCl_6, (*b*) $Na_3Co(NO_2)_6$, (*c*) K_2CrO_4, (*d*) H_2S and $(NH_4)_2S$? 6. Compare Tl' salts with Pb salts and salts of the alkalies. 7. How may Tl' salts be oxidized? 8. (*a*) Compare the action of HCl and KOH upon solutions of Tl' and Tl''' salts; (*b*) What happens when a solution of $TlCl_3$ is shaken with ether? 9. Show how Tl''' salts may be reduced. 10. Describe the flame and spectroscopic tests for Tl. 11. In what general class of minerals are Ga and In found? 12. Describe the methods briefly by which they may be separated from their mineral associates. How did you identify the presence of In in a residue from the purification of Zn? 13. Give the symbols of the oxides, chlorides, nitrates, sulphates and alums. 14. Discuss the similarities between Ga, In and Al. 15. What happens when a solution of an In salt is boiled with NH_4HSO_3? 16. Describe the spectroscopic test for In. 17. What peculiar physical property has the element Ga?

VI.

TITANIUM AND GERMANIUM.

1. What are the chief mineral sources of the element Ti? 2. In what animal and vegetable products has Ti been found? 3. Give two methods for the extraction from a mineral source. 4. Discuss the preparation and properties of the element. 5. Show how compounds of the condition of oxidation represented by the oxides Ti_2O_3 and TiO_3 may be obtained from TiO_2. 6. How are ortho- and metatitanic acids formed? 7. What happens (*a*) when a solution of $Ti(SO_4)_2$ is treated with Na_2HPO_4? (*b*) When H_2O_2 is added before the Na_2HPO_4? (*c*) When Na_2SO_3 is added after H_2O_2 and Na_2HPO_4? 8. Discuss the color tests for Ti. 9. What happens when a solution of $TiCl_4$ is shaken with ether? 10. Name the chief commercial applications of Ti. 11. What led Winkler to the discovery of Ge? 12. What are the chief mineral sources of the element Ge? 13. Give briefly the method of extraction. 14. Give symbols for some of the chief compounds. 15. Discuss similarities between Ge and C, Si, and Sn.

VII.

VANADIUM, NIOBIUM AND TANTALUM.

1. What are the chief mineral sources of V? 2. How would you obtain ammonium vanadate from vanadinite? 3. Discuss the formation of sodium vanadate from carnotite $(VO_2)_2K_2V_2O_8$. 4. How may V_2O_5 be obtained from ammonium vanadate? 5. Give symbols for the ortho-, meta- and pyrovanadates. 6. Discuss the preparation and properties of the vanadates of Ag, Pb and Ba. 7. Give symbols for the oxides of V and discuss their acidic and basic character. 8. Show how compounds of V_2O_5 may be reduced, and how compounds of V_2O_4 may be oxidized. 9. What happens when an alkaline solution of a vanadate is saturated with H_2S? 10. What are some of the important commercial applications of the element V and of its compounds? 11. Name the chief mineral sources of the elements Nb and Ta. 12. Discuss the decomposition of Nb and Ta minerals by potassium bisulphate. 13. Taking the symbol $(Fe,Mn)(Nb,Ta)_2O_6$ as that of columbite, discuss with equations the extraction of Nb and Ta. 14. Discuss the preparation and properties of the elements. 15. Show how by the action of KOH upon Nb_2O_5 potassium hexaniobate may be formed, and how by the action of KOH upon Ta_2O_5 a hexatantalate and a metatantalate may be obtained. 16. Discuss any differences between the elements Nb and Ta.

17. What commercial application has been made of the element Ta? 18. What evidence have we that Nb and Ta exist in other conditions of oxidation than that represented by the oxides Nb_2O_5 and Ta_2O_5?

VIII.

MOLYBDENUM, TUNGSTEN, URANIUM.

1. What are the chief mineral sources of the element Mo? 2. Describe a process for the preparation of MoO_3 from molybdenite. 3. How would you obtain the same oxide from wulfenite? 4. Discuss the preparation and properties of the element. 5. Name the chief oxides of Mo and classify as to their acid or basic character. 6. What happens when MoO_3 is treated with NH_4OH and the product is treated with a solution of a Ba, Pb or Ag salt? 7. Describe the action of H_2S upon an acidified solution of an alkali molybdate; the action NH_4OH+H_2S upon a solution of a molybdate. 8. Discuss the action of typical reducing agents upon Mo solutions. 9. Describe the following color tests for Mo: (*a*) H_2SO_4 conc.; (*b*) Zn+KSCN. 10. What commercial applications have been made of Mo and its compounds? 11. What are the chief mineral sources of the element W? 12. Describe a method by means of which you obtained WO_3 from wolframite. 13. What happens when WO_3 is acted upon by NH_4OH, KOH or NaOH. 14. Starting with the alkali tungstates show how tungstates of Ag, Pb and Ba may be formed. 15. Show how by the action of WO_3 upon Na_2WO_4 a metatungstate may be formed. 16. Discuss the action of H_2S and NH_4OH upon tungstates, and the action of acid upon the sulphosalt. 17. Give symbols for the chief oxides of W and some of the salts corresponding to the conditions of oxidation represented. 18. Describe the phenomena accompanying the action of reducing agents upon tungstates. 19. Discuss preparation and properties of the element W. 20. Discuss the important commercial application of elementary W and W compounds. 21. What are the chief mineral sources of the element U? 22. How did you extract U salts from pitchblende? From carnotite? 23. Discuss the preparation and properties of the element U. 24. What happens (*a*) when a uranyl salt (UO_2Cl_2) is treated with KOH or NH_4OH? Equations. (*b*) When Na_2O_2+NaOH are added to a salt of U. 25. How does $(NH_4)_2CO_3$ act upon the uranates of Na, K or NH? 26. Discuss the action of Na_2CO_3, $(NH_4)_2S$, Na_2HPO_4 and $K_4FeC_6N_6$ upon uranyl salts. 27. Discuss the color reactions of uranyl salts. 28. Discuss the reduction of uranyl salts to uranous salts and the oxidation of

uranous salts to uranyl salts. 29. Discuss the differences in chemical behavior between uranyl and uranous salts. 30. To what commercial uses has U been applied?

IX.

SELENIUM AND TELLURIUM.

1. What are the chief mineral sources of selenium compounds? 2. In what commercial residues is Se often found? 3. Describe two typical processes for the extraction of Se. 4. How did you prepare H_2SeO_3 from Se? 5. How is H_2SeO_4 prepared from Se and from H_2SeO_3? 6. Discuss the preparation and properties of $BaSeO_3$ and $BaSeO_4$. 7. How is H_2SeO_4 reduced to H_2SeO_3 and H_2SeO_3 to Se? 8. Discuss the preparation and properties of H_2Se and the selenides. 9. What is KSeCN, how is it formed, and what is the action of HCl upon it? 10. Discuss the preparation and properties of the allotropic forms of Se? 11. How is $SeSO_3$ prepared and what is the action of water upon it? 12. To what commercial uses has Se been applied? 13. What observation led to the discovery of Se? 14. Discuss the behavior of Se on being subjected to heat. 15. What are the chief mineral sources of Te compounds. 16. In what commercial residues is Te often found? 17. Describe two typical processes for the extraction of Te. 18. How did you prepare TeO_2 from Te? 19. How did you prepare K_2TeO_3 from TeO_2? 20. Discuss the preparation of H_2TeO_4. 21. How is $TeCl_4$ formed, and what is the action of water upon it? 22. How is TeI_4 formed? 23. How is H_2TeO_4 reduced to H_2TeO_3? 24. Discuss with equations the preparation of the basic sulphate and nitrate of Te. 25. How did you precipitate the element Te? 26. Discuss the action of KCN upon Te and the action of air upon the product. 27. What happens when strong H_2SO_4 acts upon Te, and when the product is treated with water? 28. What is the behavior of Te compounds on charcoal before the blowpipe? 29. Discuss the preparation and properties of H_2Te and the tellurides.

X.

PLATINUM AND THE PLATINUM METALS, GOLD AND THE RARE INERT GASES OF THE ATMOSPHERE.

1. In what forms are the metals of the Pt group generally found in nature? Name the members of the group. 2. Name a mineral source (*a*) of Pt, (*b*) of Ru. 3. Describe (*a*) a fusion process and (*b*) a wet proc-

ess by which Pt alloys may be attacked. 4. Discuss the action of the acids upon Pt and the Pt metals. 5. Which of the Pt group of metals has the lowest and which the highest fusing point? 6. How in general may the metals of this group be obtained from their salts? 7. Discuss the action of (*a*) H_2S, (*b*) $(NH_4)_2S$, (*c*) NaOH and (*d*) NH_4Cl upon solutions of the salts of the Pt metals, e.g., chlorides. 8. Mention the technical uses to which Pt and the Pt metals have been put. 9. Show by the symbols of the oxides the chief conditions of oxidation in which Pt and the Pt metals are known. 10. Discuss the occurrence of gold. 11. Describe briefly six methods of extraction. 12. Discuss the chemical and physical properties of the metals. 13. Name the two conditions of oxidation and give symbols for the oxides. 14. What happens when $AuCl_3$ is acted upon by the following reagents: (*a*) H_2S, (*b*) KI, (*c*) NH_4OH, (*d*) $SnCl_2$, (*e*) $FeSO_4$, (*f*) $H_2C_2O_4$, (*g*) $KOH+H_2O_2$. 15. Discuss the action upon metallic gold of (*a*) aqua regia, (*b*) chlorine or bromine, (*c*) potassium cyanide. 16. Discuss briefly the observations which led to the discovery of argon. 17. Discuss briefly the observations which led to the discovery of helium. 18. How were krypton, xenon and neon discovered? 19. Discuss briefly the occurrence of these gases. 20. Discuss briefly the extraction. 21. Make a comparative table showing the density, boiling points and spectra of these gases.

ANALYTICAL PART.

I.

Show how by the use of HNO_3, HCl, H_2S, NH_4OH successively upon individual solutions of salts of the following elements they may be classified into groups: Tl', W, Au, Pt, Te, Se, Mo, Ge, Ir, Ru, Rh, Os, Pd, V, Ce, Pr, Nd, Y, Th, Zr, Be, Ti, Ta, Nb, Ga, In, Tl''', U, Li, Rb, Cs.

II.

TIN AND TUNGSTEN GROUP.

1. What happens when a solution containing Ta, Nb, W, Si and Sn is evaporated to dryness with HNO_3? 2. What happens when the oxides of Ta, Nb, W, Si and Sn are treated with HF and the solution evaporated to the fuming point with H_2SO_4? 3. Discuss the action of $NH_4OH + (NH_4)_2S$ upon the residue after removal of SiO_2. 4. How does a mixture H_2O_2 and HCl act upon Nb_2O_5 and Ta_2O_5? 5. How do we detect (*a*) Ta (*b*) Nb? (*c*) W?

III.

HCl GROUP.

1. What rare basic ion may be precipitated from a nitric acid solution by HCl? 2. Is TlCl completely precipitated by HCl? How shown? 3. How do we separate Tl from Hg_2 and Ag? From Pb? 4. Which is the more insoluble, TlCl or TlI? 5. How does HCl act upon solutions containing Tl'''? 6. What oxidizing agents change Tl' to Tl'''? 7. How may Tl''' be reduced to Tl'? 8. Comment upon the solubility of TlCl in water and in HCl. 9. Comment upon the solubility of TlI in water and in KI.

IV.

H_2S GROUP.

1. Name the rarer elements which are precipitated by H_2S in acid solution. 2. Why is H_2S passed, first in hot strongly acid, and then in

cold dilute solution? 3. Which of the sulphides are best precipitated under gentle pressure and how is this accomplished? 4. Which of the sulphides are dissolved by $(NH_4)_2S$? 5. How did we separate Pt from As, Se, Te, Au and Mo? 6. Why is K_2PtCl_6 washed with KCl rather than with water, and how is the presence of Pt confirmed? 7. What happens when a solution containing Au, Se, Te and Mo is warmed with oxalic acid? 8. Why is oxalic acid used rather than H_2SO_3? 9. What happens when a solution containing Te and Se is strongly acidified with HCl and treated with Na_2SO_3? 10. Why is KI added to the diluted solution containing Te after the removal of the Se? 11. How is Mo detected and what is the compound formed? 12. How did we separate Pt and Au from the residue from the $(NH_4)_2S$ treatment?

V.

Pt GROUP.

1. Name the metals of the platinum group. 2. How is this group subdivided after the fusion with Na_2O_2? 3. How do we separate Pt from Rh? 4. What does a colorless solution after the extraction of the Na_2O_2 fusion indicate?—a blue solution?—a yellow solution? 5. How do we separate Ru and Os from Ir and Pd? 6. How are Ir and Pd detected? 7. How may Ru and Os be detected when present together?

VI.

NH_4OH AND $(NH_4)_2S$ GROUP.

1. Name the rarer elements, exclusive of the rare earth group, which are precipitated by $(NH_4)_2S+NH_4OH$. 2. How may these elements be divided into two groups by the action of $NaOH+Na_2O_2+Na_2CO_3$? 3. What happens when a solution of the chlorides of Ti, Zr, and Tl is shaken with ether? 4. How may Tl be detected in the presence of Fe? 5. How did you separate Zr and Ti? 6. Why are H_2O_2 and Na_2SO_3 used in the separation and detection of Ti as the phosphate? 7. What happens when a solution containing U, V, and Be is treated with a slight excess of $NaHCO_3$ and warmed upon a steam bath? 8. How may Be and Al be separated? 9. How did we separate U from V and confirm its presence? 10. How did we test for the presence of V?

VII.

RARE EARTH GROUP.

1. At what point in the analysis are the rare earths precipitated? 2. What is the action of HF or NH_4F upon a solution containing the rare earths? 3. How may the rare earths and alkali earths be separated if present together as fluorides? 4. Discuss the action of $Na_2S_2O_3$ upon a solution containing Ce, Y and Th. 5. How may the presence of Th be confirmed? 6. What happens when a solution containing Ce and Y is saturated with K_2SO_4 or Na_2SO_4? 7. How may the presence of Ce be confirmed? 8. How did we test for Y? 9. Discuss briefly a method for the separation of the other members of the Ce group. 10. Discuss the separation of the Y group.

VIII.

ALKALI GROUP.

1. What happens when a solution of the chlorides of the alkalies is dehydrated with amyl alcohol? 2. How do we confirm the presence of Li? 3. How may the alkali chlorides be converted into the carbonates? 4. How may the carbonate of Cs be separated from the other alkali carbonates? 5. How may we confirm the presence of Cs? 6. How may Rb and K be separated from Na? 7. Suggest a method for the separation of Rb and K. 8. Describe the spectroscopic tests for Na, K, Li, Cs, and Rb. 9. How may the alkali salts be converted into sulphates? 10. How may the sulphates be converted into carbonates?

Given a solution which may contain one of the following elements: Ta, Nb, W, Tl^{I} or ^{III}, Au, Pt, Se, Te, Mo, V, U, Zr, Th, Ce, Y, Ti, Be, Cs, Rb, Li.

A. Add HCl to acidity but not in large excess. Formation of a precipitate indicates Ta, Nb, W or Tl^{I}. (Note: gentle warming makes H_2WO_4 more insoluble; H_2TeO_3 may be precipitated from K_2TeO_3, but dissolves in excess.)

If the precipitate dissolves on warming, Tl^{I} is indicated. Confirm by other tests on original solution.

If Tl^{I} is not indicated, add a piece of Zn to the acidified solution and enough HCl to insure a good evolution of H_2. Blue color indicates W. Violet color indicates Nb. Absence of color indicates Ta. Confirm if possible by other tests on original solution.

B. If no precipitate appeared on addition of HCl, add H_2S. Brown to black indicates Au, Pt, Te, Mo; yellow to red indicates Se. White sulphur with blue solution indicates V. White sulphur with colorless solution indicates Tl^{III}. Identify by following tests on original solution: Au by $FeSO_4$ or by H_2O_2+NaOH=metallic gold; Pt by KI=reddish violet color; Te by $SnCl_2$=black Te; Se by $Na_2S_2O_3+HCl$=red Se; Mo by Zn+HCl+KSCN=red $Mo(SCN)_4$; V by NH_4OH+H_2S=red NH_4VS_3; Tl^{III} by NH_4OH=brown precipitate, $Tl(OH)_3$. Confirm by all possible tests.

C. If no precipitate occurs with H_2S, boil out H_2S, cool, add NH_4OH to alkaline reaction. Yellow precipitate indicates U. Brown indicates Tl^{III}. White indicates Zr, Th, Ce, Y, Ti or Be. If the precipitate is white, dissolve in least possible amount of HCl and add $H_2C_2O_4$. White precipitate indicates Y, Ce, Th(Zr). No precipitate indicates Ti, Be, Zr. Identify as follows: Ce by $NaOH+H_2O_2$=yellow-brown $Ce(OH)_6$. Th by solubility of oxalate in $(NH_4)_2C_2O_4$.; Y by negative results with last two tests; Ti by yellow to red color with H_2O_2; Be by precipitate with NaOH soluble in excess; Zr by negative results with last two tests and precipitation with Na_2HPO_4. Confirm all by possible tests, including tests for U and Tl.

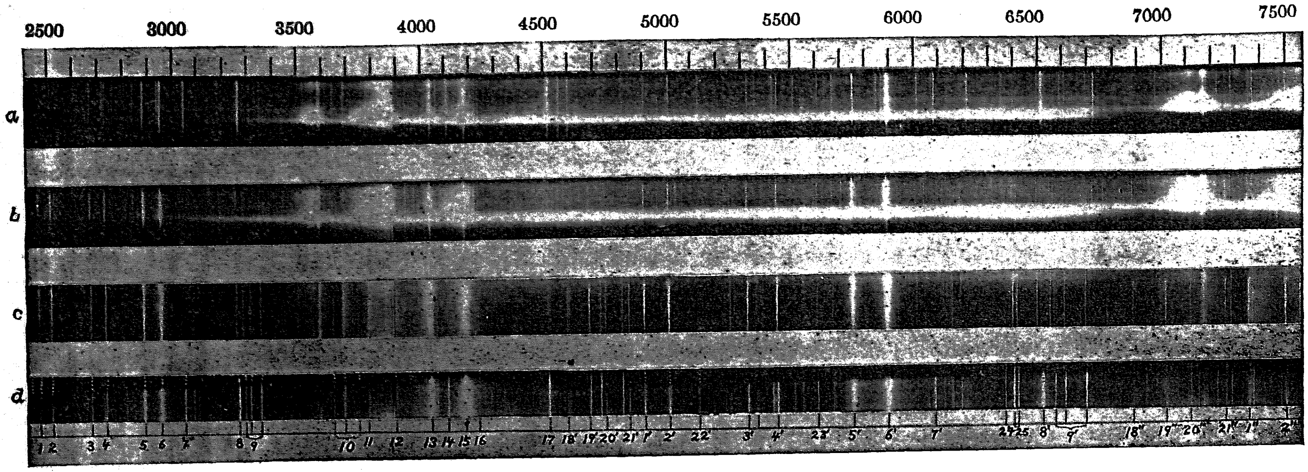
D. If no precipitate was formed by NH_4OH, treat the original solution with $Na_3Co(NO_2)_6$; a precipitate indicates Cs or Rb. No precipitate indicates Li. Confirm by spectroscopic and flame tests.

NOTE.—Ge gives a white sulphide with $HCl+H_2S$. Ga and In give white precipitate with NH_4Cl+NH_4OH. $Ga(OH)_3$ is soluble, $In(OH)_3$ is insoluble in KCH; In salts give characteristic flame spectra.

TABLE SHOWING CHIEF ASSOCIATES OF THE RARE ELEMENTS IN NATURAL AND COMMERCIAL PRODUCTS

	Ag	Pb	Hg	Bi	Cu	Cd	As	Sb	Sn	Al	Cr	Fe	Ni	Co	Mn	Zn	Ba	Sr	Ca	Mg	Na	K	Li	Rb, Cs	Be	Ce, Y	Th	Zr	Ga, In	Tl	Ti	V	Ta, Nb	Mo	W	U	Se	Te	Pt	Au	Si	S	P
Li.....										*		*			*						*	*		*	*																*		*
Rb, Cs.										*		*			*					*	*	*	*		*																*		
Be......										*		*			*				*		*					*							*								*		*
Ce, Y..									*	*		*			*			*	*	*	*				*		*	*			*		*			*					*		*
Th....																										*		*			*		*			*					*		*
Zr.....												*							*		*					*	*				*		*								*		
Ga, In .	*	*			*				*	*		*			*	*											*															*	
Tl.....	*	*			*		*					*				*						*	*	*												*	*					*	
Ti.....		*						*		*		*			*		*		*	*	*	*				*	*	*					*								*		
Ge.....	*	*			*	*	*		*							*													*		*		*								*	*	
V......		*		*	*							*				*			*		*	*														*					*	*	
Ta, Nb.								*				*			*				*		*					*	*	*			*										*		
Mo....		*										*							*	*				*											*							*	
W.....		*			*							*			*				*														*	*									
U.....		*		*	*		*										*		*			*				*					*	*	*								*	*	*
Se.....	*	*	*	*	*		*					*																		*								*				*	
Te.....	*	*	*	*	*		*	*				*	*																								*			*		*	
Pt.....		*	*		*		*					*																			*									*	*		
Au....	*	*	*	*	*							*																										*				*	

ARC SPECTRA OF SOME GALLIUM AND INDIUM PRODUCTS.*



a and *b* show the spectra of the more and less soluble ends of a series obtained by ten fractional crystallizations of the mixed caesium alums of gallium and indium prepared from the gallium-indium alloy (page 84); *c* shows the spectrum of a specimen of electrolytic gallium, and *d* the spectrum of a specimen of the original alloy.

The following numbers show the position of the chief lines of Ga, In, Pb and Zn:

18′, 18″, 19′, 19″, 20′, 20″, 1, 1′, 1″, 2, 2′, 2″, 3, 3′, 4, 4′, 5, 5′, 6, 6′, 11, 12, 13, 15, 25=Ga. 22′, 7, 7′, 8, 8′, 14, 17=In. 23′, 10 =Pb. 23′, 9, 9′, 24=Zn.

The lines having no accents are of the first order of the concave grating, those having single and double accents are of the second and third order.

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* **Uhler and Browning, Amer. Jour. Sci. [4] XLII, 389.**

MINERALS AND REAGENTS USED IN THE STUDY OF THE RARER ELEMENTS.

A. Minerals and Commercial Residues from which the Rarer Elements are extracted:

Li, Lithiophilite; Cs and Rb, Lepidolite; Be, Beryl; Ce, Cerite or Monazite Residues from the extraction of Thorium; Y, Gadolinite; Th, Monazite or Welsbach Mantle Ash; Zr, Zircon; Ga and In, Leady Residue from the Purification of Zinc; Tl, Flue Dust; Ti, Rutile or Illmenite; Ge, Germaniferous Zinc Oxide; V, Carnotite or Patronite; Cb (Nb) and Ta, Columbite; Mo, Molybdenite; W, Wolframite or Hübnerite; U, Pitchblende or Carnotite; Se and Te, Copper Refining Residues; Pt, Platinum Residues; Au, Gold Ore.

B. Reagents:

Acids—Sulphuric, Hydrochloric, Nitric, Acetic, Oxalic, Orthophosphoric, Tartaric, Sebacic, Tannic, Gallic, Pyrogallic, Chloroplatinic.

Ammonium Compounds—Hydroxide, Carbonate, Chloride, Sulphide, Acetate, Oxalate, Acid Sulphite, Sodium Hydrogen Phosphate, Alum.

Sodium Compounds—Hydroxide, Carbonate, Acid Carbonate, Sulphate, Sulphite, Thiosulphate, Fluoride, Hypochlorite, Hydrogen Phosphate, Dioxide, Cobalti-Nitrite.

Potassium Compounds—Hydroxide, Bromide, Iodide, Sulphate, Ferrocyanide, Cyanide, Ferricyanide, Chloride, Acid Sulphate, Nitrite, Iodate, Formate, Sulphocyanide, Chromate, Carbonate, Permanganate.

Aluminum Sulphate, Antimony Trichloride, Barium Carbonate, Barium Chloride, Bromine Water, Calcium Fluoride, Copper Sulphate, Ferrous Sulphate, Ferric Chloride, Hydrogen Dioxide, Lead Acetate, Lead Dioxide, Magnesium, Mercurous Nitrate, Stannous Chloride, Stannic Chloride, Silver Nitrate.

Amyl Alcohol, Ethyl Alcohol, Carbon Bisulphide, Charcoal, Starch, Asbestos Fibers, Litmus Paper, Turmeric Paper.

Generators—Hydrogen Sulphide, Carbon Dioxide, Hydrochloric Acid, Chlorine.

Special Organic Reagents—Diphenylcarbazid, Hydrazine Sulphate, Morphia, Nitroso-beta-naphthol, Phenylhydrazin, Thiourea.

Compounds of the Rarer Elements which it is desirable to have on hand:

Nitrates or Chlorides of Li, Cs, Rb, Be, Y, Ce, La, Pr, Nd, Th, Zr.

Chlorides of Au, Pt, Pd, Ru.

Nitrates of Tl, U.

Oxides: TiO_2, Nb_2O_5, Ta_2O_5, MoO_3, WO_3, SeO_2, TeO_2.

Ammonium Vanadate, Sodium Rhodium Chloride, Sodium Iridium Chloride, Potassium Osmium Chloride.

Apparatus.

A set of apparatus which would be issued for a course in Qualitative Analysis would cover the needs of this course. A spectroscope or two should be on hand for observation of flame and absorption spectra.

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